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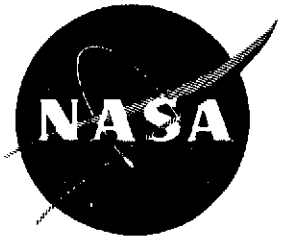

FABRICATION AND TEST OF INORGANIC/ORGANIC SEPARATORS

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16. Abstract

Work on this contract was performed under two major tasks. In Task I, completion of testing and failure analysis of MDC 40 Ahr silver-zinc cells containing largely inorganic separators was accomplished. The results showed that the wet stand and cycle life objectives of the silver-zinc cell development program under Contracts NAS 3-10928 and NAS 3-15686 and the present contract were accomplished and led to recommendations for cell composition, design and operation that should provide further improvements in cycle and wet life.

In Task II, the paramount task, the building, testing and failure analysis of two-plate cells employing three optimum separators selected on the basis of extensive screening tests on Contract NAS 3-15686, was performed. The best separator material as a result of these tests was doped calcium zirconate. This result points to the potential of building of silver-zinc cells having longer cycle and wet life and a longer period of capacity retention than cells heretofore made with inorganic separators.

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CONTENTS

CONTENTS (Concluded)

LIST OF ILLUSTRATIONS

Figure

LIST OF ILLUSTRATIONS (Concluded)

Figure

LIST OF TABLES

Table

LIST OF TABLES (Concluded)

SUMMARY

The work on this contract was done under two major tasks.

The first task was to continue testing and failure analysis of 40 Ahr silver-zinc cells containing semiflexible inorganic separators developed at McDonnell-Douglas Corporation (MDC) under Contract NAS 3-10928 and tested by SRI under Contract NAS 3-15686. The data accumulated by MDC and SRI indicate that the major objective of the program--the development of a heat-sterilizable, sealed silver-zinc cell capable of extended stand and subsequent cycling--was accomplished. Cells that were placed on discharged stand and then cycled, plus a small group of cells that were cycled immediately after activation, both yielded high cycle and wet lives. Although charged stand and float-charged stand are detrimental standing conditions, useful working lives are achievable by standing conditions at subambient temperatures.

Analysis of the data showed that cell failures were almost exclusively from shorting zinc nodules, and filamentary or leafy zinc dendrites. Although silver was found in the separators, no shorting was traced to continuous paths of silver. The low incidence of slumping indicates the potential advantages of using MDC type cells to achieve extended life in batteries containing zinc electrodes and alkali electrolyte. Recommendations to improve silver-zinc cells include suggested environmental and electrical conditions for standing and operating cells, exploration of factors that cause separator degradation, and suggestions for improved separators.

The major task in this investigation was to build and test two-plate cells, using battery separators fabricated from separator

compositions selected by a series of screening tests from a large number of compositions on a previous program (Contract NAS 3-15686). After cell testing and subsequent failure analysis, the best separator material--a doped calcium zirconate--was then selected to be used as a control in a second series of tests. Modifications in the doping level of this separator material were made and tested in two-plate cells, in anticipation of finding an optimum separator. The final results indicated that the original doping level in the calcium zirconate provided the best separator material. This material, when incorporated in separators gave improved life characteristics to cells compared to all other separators, including the separators used in the 40 Ahr MDC cells.

INTRODUCTION

Silver-zinc batteries, which have higher energy densities than other alkaline batteries, are attractive energy sources for compact power applications, especially for space applications. However, limited cycle- and wet-stand life and sealability problems have been deterrents for some applications.

As demonstrated in a series of silver-zinc battery development programs supported by NASA (References Nos. 1 to 7), the development of inorganic battery separators represents a major advance toward the goal of long-life, hermetically sealed batteries. The usefulness of these separators was confirmed by the results of this SRI study. Many sealed silver-zinc cells (nominally 40 Ahr) were still cycling more than three years after their construction and initial testing. The results obtained from cycling of these cells and analysis of those cells that failed were given under Task I in report NASA CR-121215. The results obtained on cells that failed since then are given under Task I in this report.

Preliminary results of development programs at the former Astropower Laboratory of the McDonnell-Douglas Corporation suggested that any improvements in inorganic separators and silver-zinc battery characteristics were likely to occur through modifying existing technology. Achieving such improvements was the overall objective of the current program. The specific objective was to develop separator formulations with improved characteristics (such as better chemical compatibility, and a negligible rate of gassing when in contact with zinc) that would permit increases of stand and cycle life of alkaline cells, especially

silver-zinc cells. Twenty different materials (including the 3420-09 and 3420-25 reference materials) were previously prepared and tested[7] as rigid separators, and 16 of these materials were processed into semiflexible separators.

From these 16 materials, three of the most promising materials plus a reference material (3420-25) were selected for initial tests as separators in two-plate cells on the basis of previous screening tests.[7] The three materials were: (1) material B′, a proprietary, synthetic. substituted olivine, (2) material JC, a commercial magnesium titanate, and (3) material S′, a proprietary, doped calcium zirconate.

A second series of tests using two-plate cells was conducted after an evaluation of the cells in the first series. Material S′ was selected as the most promising material in the first series of tests. This material was also tested in the second series of tests. The other materials used in the second test series were undoped calcium zirconate and a heavily doped (approximately twice the dopant level of S′) calcium zirconate. In addition, the zinc electrodes of a group of three cells with calcium zirconate separators were treated with lead acetate ($\sim$ 28 mg Pb per plate) to measure whether zinc dendrite penetration was inhibited.

This report contains the results of the cell testing of inorganic separator materials selected on the basis of previous screening tests, and also contains the results of continued testing of silver-zinc cells fabricated under a previous NASA contract (NAS 3-15686).

EXPERIMENTAL PROCEDURE

The Work Statement for NASA Contract NAS 3-17344 specified that SRI was to continue testing silver-zinc cells fabricated and placed on various long-term tests under Contract NAS 3-10928, continued on Contract NAS 3-15686, and further continued under the present contract. The cells were to be tested, according to the established schedule, until the cells failed or until the end of the contract.

The work statement also called for analysis of all cells that were tested to failure in this program. Failed cells were to be disassembled, the causes of failure were to be determined by examining the cells using appropriate techniques, and failure analysis data were to be transmitted to the NASA project manager.

During this program, SRI and the NASA project manager jointly decided that some cells that failed in testing at SRI would be analyzed at NASA-Lewis. Complete data on all failed cells analyzed at SRI were to be transmitted to the NASA project manager as appendices to the Monthly Progress Reports.

Furthermore, SRI was to formulate separator materials of the three materials previously selected under Contract NAS 3-15686, fabricate materials into battery separators, assemble these separators into cells, and then test the cells. After analysis of the cell test data, a further selection of materials was to be made, and these materials were to be fabricated into battery separators and assembled into cells for testing.

Testing of Original MDC Cells

The testing regimes for the cells remaining on test or requiring failure analysis after completion of Contract NAS 3-15686 are shown in Table 1. These regimes are the same ones used under the above cited contract.

Battery Separator Preparation

All separators used in the two-plate cells were prepared according to the proprietary procedures developed at McDonnell-Douglas Corporation, except where minor modifications, such as mechanically dipping the separator bags, resulted in improved battery separators.

Battery separators were made in the form of a bag or envelope from specially treated fuel cell asbestos. These bags were then coated with a uniform 0.005-inch thick layer of the separator material by dipping the bags in a slurry of the appropriate material. The actual thickness was held to 0.127 $\pm$ 0.025 mm.

The slurries were prepared according to established procedures. All inorganic powders were screened through a 325-mesh screen to remove tramp material and agglomerates. A slurry was made up from inorganic material, resinous binder, plasticizer, and solvent, and mixed in a ball mill for from 15 to 16 hours. The slurry was then screened through a 325-mesh sieve to remove agglomerates of ceramic material and undissolved polymer, and chips from the mill-mixing media. After these steps, the viscosity was adjusted if necessary, and the slurries were bottled for subsequent use in the dipping operation. The compositions and procedures essentially followed those cited in U.S. Pat. No. 3,625,770. No extraordinary problems were encountered in preparing the slurries.

Table 1

CYCLING REGIMES

Conditions / Regime Code (% DOD)	Cycling Period	Frequency	Discharge	Charge	Charging Voltage Limit (per cell)
VK-1 (10)	24 hr	one cycle/day	2A for 2 hr	0.32A for 22 hr	2.02
VK-2 (7.5 & 15)	24 hr	2 different cycles per day, (a) & (b)	(a) 3A for 1 hr (b) 3A for 2 hr	(a) 0.45A for 7 hr (b) 0.45A for 14 hr	2.00
100% DOD (NHS-114 Series)	1 mo.	1 cycle followed by charged stand for 1 month	10A to 1.00V, followed by 2A to 1.00V	1.5A to 2.00V limit	2.00
100% DOD (HS-54-5,6, & HS-123-GX)	defined by charge-disch. conditions	as frequently as convenient, with charged stand between cycles	6A to 1.00V, followed by 2A to 1.00V	1.5A to 2.00V limit	2.00
Modified (10.5) VK-1 (HS-16 Series)	24 hr	one cycle per day	0.5A for 2 hr	0.06A for 22 hr	2.02

Slurries of materials B′, JC, Q (3420-25), and S′ were prepared according to the above cited procedure. Material B′ is a proprietary, synthetic, substituted olivine; material JC is a commercial magnesium titanate; Q (3420-25) is a zirconia-based proprietary material, and S′ is a proprietary doped calcium zirconate. These four materials were used to prepare slurries for the first series of 12 two-plate cells, with three cells fabricated per material.

The second series of 12 cells had separators made from material P (commercial calcium zirconate), S′, and SS. Material SS had approximately double the dopant content present in material S′. Enough separators were made to assemble six cells having P separators (three of these cells coded PX, following a NASA suggestion). These separators had their negative plates treated with approximately 28 mg of Pb (as acetate) per plate so that zinc dendrite penetration through the battery separator could be noted. Three cells each were assembled with S′ and SS separators.

One pilot cell was also assembled for each series of tests. The pilot cell in the first series contained Q material separators; the pilot cell in the second test series contained S′ material separators. The pilot cells were used to determine electrolyte requirements, to verify the selected cycling regimes, to measure the internal impedance, and to monitor the gas pressure before activating the test cells and during testing of the 12 test cells.

Cell Assembly

Cell cases and lids (provided by NASA) made of glass-filled PPO resin were used as the containers. These containers, which were 14.1 x 9.2 x 3.4 cm, were of the type used in the nominal 40 Ahr cells fabricated at MDC on previous programs. The cell lips and lid edges

were lightly abrasive-blasted to deglaze and clean the surfaces that would be in contact with the RTV rubber sealant. The cases were washed in deionized water and dried with warm air before the internal components were installed in them. Before blasting the lids, it was necessary to pre-tin the upper portion of the silver-plated, hollow-steel terminal posts.

The respective electrodes were very carefully inserted into the preshaped separator bags. A U-shaped Teflon sling enclosing one positive and one negative electrode was sandwiched between two plastic shims of appropriate thickness. The assembly was then gently pushed into the cell case. The electrode pack fitted snugly in the cell case, with very little excess void volume. The tabs were passed through the hollow electrode posts of the lids, whose edges were precoated with RTV silicone rubber (the cell lips were also precoated with RTV rubber), and the lids were seated. The extruded RTV rubber was molded into a neat fillet along the edges. After a half-day cure, the tabs were soldered to the posts, making a complete solder seal over the posts, after gently scavenging acetic acid vapors (from the RTV rubber) with a gentle stream of clean air passing into the cell.

All cells of the first series were activated with 45% KOH (approximately 35 to 36 cc) as determined from the pilot cell. This quantity was established to make a final electrolyte level (vacuum filling and one day soak) that would be about 3 to 4 mm below the tops of the bags. As requested by NASA, the second series were activated with a 30 cc filling of 45% KOH.

Following activation, the cells were heat-treated at $100^{\circ}C$ for 24 hours (filler plugs were installed but not sealed). After the cells were cooled from the heat treating, the filler plugs were sealed and the cells given their formation cycles: Each plug had a small drilled

hole, back filled with RTV rubber to permit blowout in case of dangerous pressures.

Cell Testing

Table 2 displays the details of the formation cycle and the regular 100% DOD continuous cycle for the first and second series of cells. All regular 100% DOD cycle testing was controlled by automatic equipment originally designed and used for testing the 40 Ahr cells on the VK-2 regime on Contract NAS3-15686. The control resistors were adjusted for the currents required by the two-plate cells.

On the regular 100% DOD cycle, the cells were charged from a constant-current power supply until each cell reached 2.050 V ± 2 mV,* at which time appropriate relays switched the cells to a constant-potential power supply, set at 2.000 V. After a lapse of 10 hours, a time clock switched all cells to the discharge position; each cell discharged through its own adjustable transistor-resistor load. A cell that reached 1.000 V ± 2 mV before the full two-hour period allotted, was automatically switched to the open-circuit position, to await the time clock switching to charge again after the lapse of the 2 hours. An electrically operated counter logged the number of cycles.

Each cell had its voltage monitored in a succession of 2-second time intervals so that the 12 test cells plus the pilot cell plus a reference-voltage signal (14 positions) would be scanned in approximately one-half minute. This arrangement allowed a maximum of only one-half minute for a cell to discharge below 1.000 V, or to charge

*The first several cycles in the first series had a limit of 2.000 ± 2 mV but was increased to 2.050 V due to inadequate charging.

Table 2

CHARGE-DISCHARGE CONDITIONS
TWO PLATE CELLS

Formation Cycle			
		Rate	Voltage Limit
Charge			
Series 1		0.30 Amps (~ C/20)	2.005 V
Series 2		0.33 Amps (~ C/20)	2.050 V
Discharge			
Series 1	A	1.1 Amps (~ C/5)	1.00 V
	B	0.55 Amps (~ C/10)	1.00 V
Series 2	A	1.34 Amps (~ C/5)	1.00 V
	B	0.69 Amps (~ C/10)	1.00 V

100% DOD Regular Cycles			
	Rate	Voltage limit	Time limit
Charge			
Series 1	0.55 Amps (~ C/10)	2.05 V. Then 2.00 V float	10 hrs
Series 2	0.57 Amps (~ C/10)	2.05 V. Then 2.00 V float	10 hrs
Discharge			
Series 1	2.42 Amps (~ C/2)	1.00 V	2 hrs
Series 2	2.71 Amps (~ C/2)	1.00 V	2 hrs

above 2.050 V before the actuating relays performed their assigned switching function. Separately, another device automatically sampled each cell's voltage successively for 6 seconds, feeding the signals to a recorder to create a graphic display. A separate 24-channel Esterline-Angus recorder sampled the current passing through each cell (each cell passed its current through its own calibrated shunt), printing out its value and identifying number. The current for any given cell was sampled once every 2 minutes.

The first series of cells received three formation cycles before commencing the regular 100% DOD cycles as defined in Table 2. After a few regular 100% DOD cycles, it became apparent that the voltage limit of 2.000V on the constant-current supply was too low because the discharge capacities were low. Approval was obtained from NASA to raise the voltage on the constant-current supply to a value permitting the cells to charge to 2.050V $\pm$ 1 mV. This increased charge improved the discharge performance of all cells. During the tests of the first series of cells, accurate discharge times and currents were determined, and discharge capacities were calculated for each cell three times per week. In this way, capacity decline with increasing cycles could be monitored. At Cycle 24, a malfunction in the charging equipment allowed the cells to receive more than the allotted charge; however, the effect was apparently not damaging.

Early in the testing (Cycle 37), samples of cell gas were withdrawn for chromatographic analysis. Because the compositions varied so widely, cell leaks were suspected but not verified during the testing. Nevertheless, a pressure transducer was fitted to the pilot cell for a short period to observe pressure excursions. Later, the transducer was fitted to Cell S-1-2. Both cells had leaks, which were sealed over with paraffin wax.

After Cycle 130, all cells were put on open-circuit stand (charged) for 4 days to check them for "slow shorts." The residual capacity was then determined. At this point, many of the cells were close to the end of life (some could cycle poorly only to Cycle 142).

The second series of cells received two formation cycles (c.f. Table 2) before commencing the regular 100% DOD cycling. In this case, the constant-current voltage limit on the cells for formation and regular 100% DOD cycling remained at the 2.050 V limit previously established. The constant-potential power supply for 100% DOD cycling was held at 2.000 V as before. Tests were controlled by the same automatic equipment used in the first series of cells.

The pilot cell was fitted with a pressure transducer to measure the pressure excursions during experimental charge and discharge conditions, when the charge voltage limit was raised to 2.100 V. Discharge capacities were determined once per week, as arranged by joint agreement by NASA and SRI. These checks provided sufficient control to enable changes to be made if needed. Cycling was continued past the capacity failure point (contractually defined as deliverance of less than 50% of the original capacity) by mutual agreement between NASA and SRI. Cycling terminated with Cycle 120. A formation charge-discharge cycle was then applied to determine the capacity of all cells followed by failure analysis.

RESULTS

The results are presented in two separate categories: (1) those that relate to the cells tested at SRI but fabricated at MDC and (2) those that pertain to the two-plate cells fabricated and tested by SRI, using the selected optimum separators.

Test Results on the Cells Manufactured at MDC

Of the 141 cycling cells transferred to SRI on Contract NAS 3-10928, 29 failed cells were returned to NASA for failure analysis and 48 were analyzed at SRI. The results were previously reported.[7] Thirty cells failed during this program and the results of the failure analyses are given below. This testing program was terminated on 10 October 1973. The 34 cells on test at that time which included 10 cells that had failed but had remained on test, will be returned to NASA.

The breakdown of all 141 cells into the various test groups and test conditions is shown in Table 3. A full description of the various test groups (and subgroups) and test conditions, together with the definitions of the objectives for these are provided in Reference 7.

Viking Cell Group (Cycling Regime: VK-2)

Although the uncertainties and variations associated with the small numbers of cells per subgroup are considerable, several major trends are apparent (Table 4), further supporting the observed trends cited in Reference 7.

Table 3

SUMMARY OF CELL TEST GROUPS AND CONDITIONS

Experimental Factor	No. of Cells	No. of Failed Cells*	Regime	Comments
3-Plate Pilot Cells	6	6	VK-1	3-plate cells; all negatives bagged; some positives bagged.
Viking	4	4	VK-2	Standard Design 7; 45 Ahr original capacity.
	17	15		Charged stand, 10°-42°C for 21+ months prior to cycling.
	15	15		Float stand at 10°-32°C for 21+ months prior to cycling.
	15	11		Discharged stand at 24°C for 21+ months prior to cycling.
	4	-	Stand	Discharged stand
Design Variation	5	4	VK-1	Design 7 ($6b^+/5b^-$); 24°C
	5	2		Design 6 ($4b^+/\ell/5b^-$); 24°C; extra separator layer between the 4 positive bags and 5 negative bags
	5	1		Design 8 ($6b^+/\ell/5b^-$); 24°C; extra separator layer between the 6 positive bags and 5 negative bags
Temperature-Battery/Cell	4	4	VK-1	Tested as a battery at 24°C
	2	2		Tested as single cells at 24°C
	4	2		Tested as a battery at 10°C
	2	2		Tested as single cells at 10°C
	3	3		Tested as a battery at 32°C
Plate Lock	4	4	VK-3	Design 7, no plate lock, environmentally tested
	4	4		Design 7, epoxy plate lock, normal cure; no environmental test
	3	3		Design 7, epoxy plate lock, normal cure; environmental test
	4	4		Design 7, epoxy plate lock, normal cure plus 24 hrs at 100°C; environmentally tested
	1	1		Design 7, GX film separator, plate lock, normal cure; environmentally tested
	20	17	100% DOD	Charged stand, discharged about once per month
	1	1	Stand	Continuous charged stand since original 3 cycles
Extra	2	2	100% DOD	Design 5 ($4b^+/L/5b^-$); extra supported separator layer between bags.
	1	0		Design 7; 8 wraps of GX film plus double plate lock
	3	3		Design 5; on 7 to 9-month stand before cycling.
	5	5		Design 3 ($5b^+/6b^-$); on 7 to 8.5-month stand before cycling.
	2	2		Design 2 ($5b^+/6b^-$); only negatives were bagged.
TOTALS	141	117		

All cells of Design 7

*†Status as of 10 October 1973.

The designs used for the cells tested under this program are described in Reference No. 6. As an example of the design notation, $6b^+/5b^-$ indicates that a cell comprises six bagged positive and five bagged negative electrodes. The letter (ℓ) indicates presence of an additional layer (usually an asbestos-free composite of binder and the inorganic material) between each pair of adjacent positive and negative electrodes. Capital letter (L) indicates that the extra layer consists of the semiflexible separator material used to fabricate separator bags.

Table 4

CYCLING RESULTS: VIKING CELL GROUP*
(Status as of 10 October 1973)

Early-Cycling Category: 4 Total Cells

No. of failed cells	4
Range and average wet life (days)	1142-1300 [1237]
Range and average of cycle life (cycles)	2004-2318 [2186]

Float Charged-Stand Category: 15 Total Cells

Subgroup standing at 10°C: total cells	5
No. of cells failing reconditioning	1
No. of cells failed in cycling	4
Range and average of wet life (days)	869-1035 [929]
Range and average of cycle life (cycles)	152- 480 [268]
Subgroup standing at 24°C	5
No. of cells failing reconditioning	2
No. of cells failed in cycling	3
Range and average of wet life (days)	903-1228 [1069]
Range and average of cycle life (cycles)	218- 885 [668]
Subgroup standing at 32°C	4
No. of cells failing reconditioning	1
No. of cells failed in cycling	974
Wet life (days)	379
Cycle life (cycles)	

Charged-Stand Category: 17 Total Cells

Subgroup standing at 10°C: total cells	5
No. of cells failing reconditioning	0
No. of cells not failed in cycling	2
Wet life (days)	1553
Cycle life (cycles)	1569-1573
No. of cells failed in cycling	3
Range and average of wet life (days)	795- 861[823]
Range and average of cycle life (cycles)	99- 209[150]
Subgroup standing at 24°C: total cells	5
No. of cells failing reconditioning	1
No. of cells failed in cycling	4
Range and average of wet life (days)	994-1107[1039]
Range and average of cycle life (cycles)	474- 699[565]
Subgroup standing at 32°C: total cells	5
No. of cells failing reconditioning	5
Subgroup standing at 42°C: total cells	2
No. of cells failing reconditioning	2

Discharged-Stand Category:† 15 Total Cells

Subgroup of virgin# standing cells	
No. of cells failing reconditioning	2
No. of cells not failed in cycling	3
Range and average of wet life (days)	1266-1486[1392]
Range and average of cycle life (cycles)	1223-1473[1389]
No. of cells failed in cycling	6
Range and average wet life (days)	1237-1507[1360]
Range and average of cycle life (cycles)	1163-1447[1260]
Subgroup of cells with charged-stand history	
No. of cells failing reconditioning	2
No. of cells not failed in cycling	1
Wet life (days)	1488
Cycle life cycles	1469
No. of cells failed in cycling	1
Wet life (days)	1474
Cycle life (cycles)	1447

*Viking group cells were cycled on the VK-2 regime, with cells at laboratory temperature (nominally 24°C).

†Discharge stand was at 24°C.

#That is, cells not cycles (except in forming step) prior to stand; this was the standard condition for all Viking cells with exception of the subgroup of discharged-stand cells with charged-stand history.

The trends are as follows:

(1) Cell survivability after reconditioning, cycle life, and wet life is higher for discharged stand (21 to 25 months) than for charged or float-charged stand (also for 21 to 25 months).

(2) Cells that are cycled soon after activation (essentially no stand period) have the best cycle life expectancy, exceeding 2000 cycles.

(3) If the standing temperature is increased, the survival rate of reconditioned charged and float-charged stand cells decreases.* The effect of standing temperature is marked: While only one of the 10 cells standing at 32°C or 42°C survived, 9 out of 10 cells survived standing at 10°C. Of the cells standing at 24°C, 7 out of 10 cells survived reconditioning.

(4) An unexpected finding was that cells surviving charged or float-charged stand at 10°C had markedly inferior cycle life compared to the subgroups standing at 24°C.

Cell Design Variation Group (Cycling Regime: VK-1)

Two of the three cell designs (Designs 6 and 8) had extra layers of separator between cell plates. As expected, the extra separator layers appear to delay cell failure in cycling. With due regard for small number statistics, this trend is noted in Table 5. Design 6 had two out of five cells fail, Design 8 had one out of five cells fail, but Design 7 had four out of five cells fail.

*Temperature influence was not investigated for the discharged stand cells.

Table 5

CYCLING RESULTS: CELL DESIGN VARIATION GROUP*
(Status as of 10 October 1973)

Design 7 ($6b^+/5b^-$) subgroup: total cells (in battery)	5
No. of cells not failed in cycling	1
Wet life (days)	1515
Cycle life (cycles)	1254
No. of cells failed in cycling	4
Range and average of wet life (days)	477-1388[991]
Range and average of cycle life (cycles)	348-1127[763]
Design 6 ($4b^+/\ell/5b^-$) subgroup: total cells (in battery)	5
No. of cells not failed in cycling	3
Wet life (days)	1515
Cycle life (cycles)	1305
No. of cells failed in cycling	2
Wet life (days)	1077-1171
Cycle life (cycles)	874- 964
Design 8($6b^+/\ell/5b^-$) subgroup: total cells (in battery)	5
No. of cells not failed in cycling	4
Wet life (days)	1515
Cycle life (cycles)	1266
No. of cells failed in cycling	1
Wet life (days)	1141
Cycle life (cycles)	892

*Cycling is on the VK-1 regime, with all cells at laboratory temperature (nominally 24°C).

Temperature-Battery/Cell Group (Cycling Regime: VK-1)

The general trend of lower temperatures (below room temperature) for cell or battery operation favors life expectancy, as notes in Table 6. The two major trends may be summarized as follows:

(1) Operation of cells in batteries appears to reduce cell wet and cycle life expectancy, presumably because of the additional stresses (excess voltage and/or overcharge) imposed on the remaining cells if one of the cells in a battery has lower voltage and charge acceptance during impending failure.

(2) Cycling of cells below room temperature appears to have a somewhat beneficial effect on wet stand and cycle life, whether cells are cycled singly or as a battery. However, this conclusion is weakened by the observation that cells from the 32°C battery group had better average cycle life than those from the 24°C battery. These findings must be considered in the light of small number statistics and the fact that impending failure of a single cell in a battery can impose very high stresses on all remaining cells. No comparison is possible for single cells since the 32°C subgroup did not include single cells.

Plate-Lock Cell Group (Cycling Regime: 100% DOD)

During environmental testing of cells under Contract NAS 3-10928, it was shown that applying high shock loads to cells caused the electrode packs to shift partly into the void space under the cell lids. Although no catastrophic cell failures were caused by environmental testing and the electrical performance of cells with shifted packs was satisfactory, an epoxy plate lock and heat sealing of bag tops (to localize electrodes within bags) were added as design features to one group of cells. Testing of this group was continued under the current program.

Table 6

CYCLING RESULTS: TEMPERATURE-BATTERY/CELL GROUP*
(Status as of 10 October 1973)

Subgroup at 10°C:	total cells	6
No. of cells cycled individually		2
No. of cells failed in cycling		2
Wet life (days)		1334 -1444
Cycle life (cycles)		1198 -1305
No. of cells cycled as a battery		4
No. of battery cells failed in cycling		2
Wet life (days)		1528
Cycle life (cycles)		1336
No. of battery cells failed in cycling		2
Range and average of wet life (days)		757-785 [771]
Range and average of cycle life (cycles)		572-598 [585]
Subgroup at 24°C:	total cells	6
No. of cells cycled individually		2
No. of individual cells failed in cycling		2
Range and average of wet life (days)		661 -1222
Range and average of cycle life (cycles)		541 -1096
No. of cells cycled as a battery		4
No. of battery cells failed in cycling		4
Range and average of wet life (days)		554-701 [591]
Range and average of cycle life (cycles)		429-576 [466]
Subgroup at 32°C:	total cells	3
No. of cells cycled as a battery		3
No. of battery cells failed in cycling		3
Range and average of wet life (days)		837-1188 [958]
Range and average of cycle life (cycles)		668-1019 [789]

*Cycling is on the VK-1 regime.

The cells of the plate-lock group were broken down into subgroups that correspond to the factors examined. These subgroups and the results obtained in cycling these cells are shown in Table 7. The capacity loss during cell operation is shown in Figures 1 to 4 as the percentage of first formation capacity versus cycle number. No group was clearly superior to any other, although the B and C subgroups tended to have higher capacity retention, at least for the first 15 (approximately) cycles. At 50% of the formation capacities of surviving cells in the B and C subgroups had an average of 27 and 30 cycles, respectively, compared to surviving cells of subgroups A and D which had 26 and 24 cycles, respectively. At 70% of the formation capacity, surviving cells of the B and C subgroups had 22 cycles each, compared to surviving cells of subgroups A and D which had 20 and 18 cycles, respectively. The reasons for variation in formation capacity are not clear. One must exercise caution in interpreting small-number statistics, especially in this case where curve smoothing methods were employed.

The anomalous dip in the curve of cell NHS-114-17 might be explained by the gradual increase in shorting Zn dendrites, to Cycle 29, followed by a gradual recession (decomposition) of the dendrites that caused the slow shorts.

In examining the cycle lives to failure, as noted in Table 7, subgroup D appears to be best, followed by subgroup C and then by subgroups A and B. The wet lives follow the same pattern. Several trends are shown by the test results:

(1) Plate locking tends to degrade the wet and cycle life of cells; the effect is not very large but definitely discernible.

(2) Extended curing of the epoxy cement used for plate locking appears to reduce the degrading effect of plate locking on cell life.

Table 7

CYCLING RESULTS: PLATE-LOCK GROUP*
(Status as of 10 October 1973)

	100% DOD
Subgroup A (epoxy plate lock, normal cure, not environmentally tested), total cells	5
No. of cells not failed in cycling	1
Wet life (days)	1160
Cycle life (cycles)	34
No. of cells failed in cycling	4
Range and average of wet life (days)	605- 925[772]
Range and average of cycle life (cycles)	16- 27[22]
Subgroup B (epoxy plate lock, normal cure, environmentally tested), total cells	5
No. of cells not failed in cycling	1
Wet life (days)	1168
Cycle life (cycles)	34
No. of cells failed in cycling	4
Range and average of wet life (days)	536- 923[771]
Range and average of cycle life (cycles)	14- 27[22]
Subgroup C (epoxy plate lock, extended cure, environmentally tested), total cells	5
No. of cells not failed in cycling	1
Wet life (days)	1166
Cycle life (cycles)	34
No. of cells failed in cycling	4
Range and average of wet life (days)	620-1013[840]
Range and average of cycle life (cycles)	17- 31[24]
Subgroup D (control: no plate lock, environmentally tested), total cells	5†
No. of cells failed in cycling	3
Range and average of wet life (days)	755-1069[918]
Range and average of cycle life (cycles)	21- 33[27]

*All cycling is at laboratory temperature (nominally 24°C).

†Two of these cells exploded on cycle 10 (wet life: 418 days) due to equipment malfunction; their wet and cycle life is not included in the data of the table.

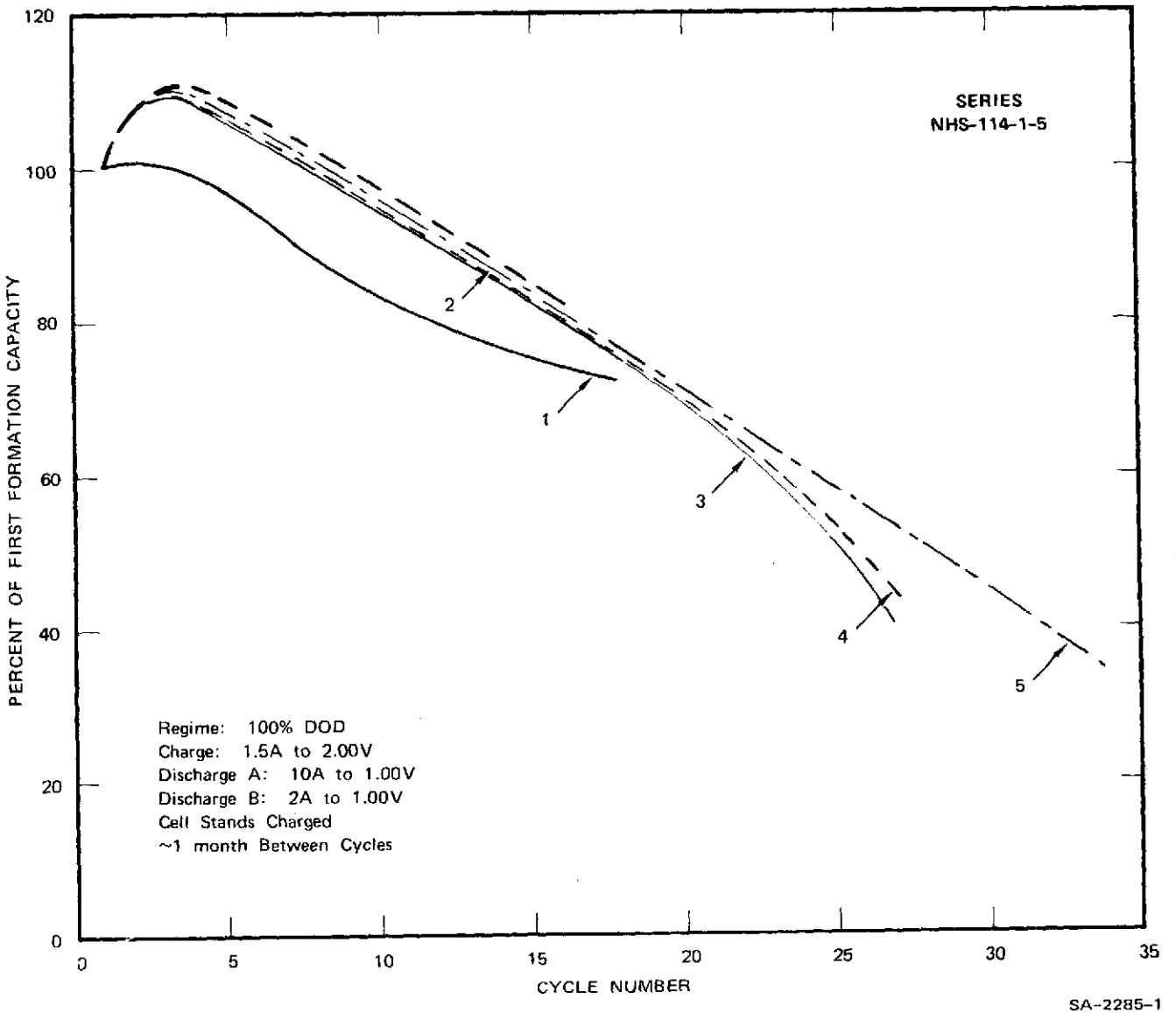

FIGURE 1 OUTPUT CAPACITY RETENTION WITH CYCLE LIFE

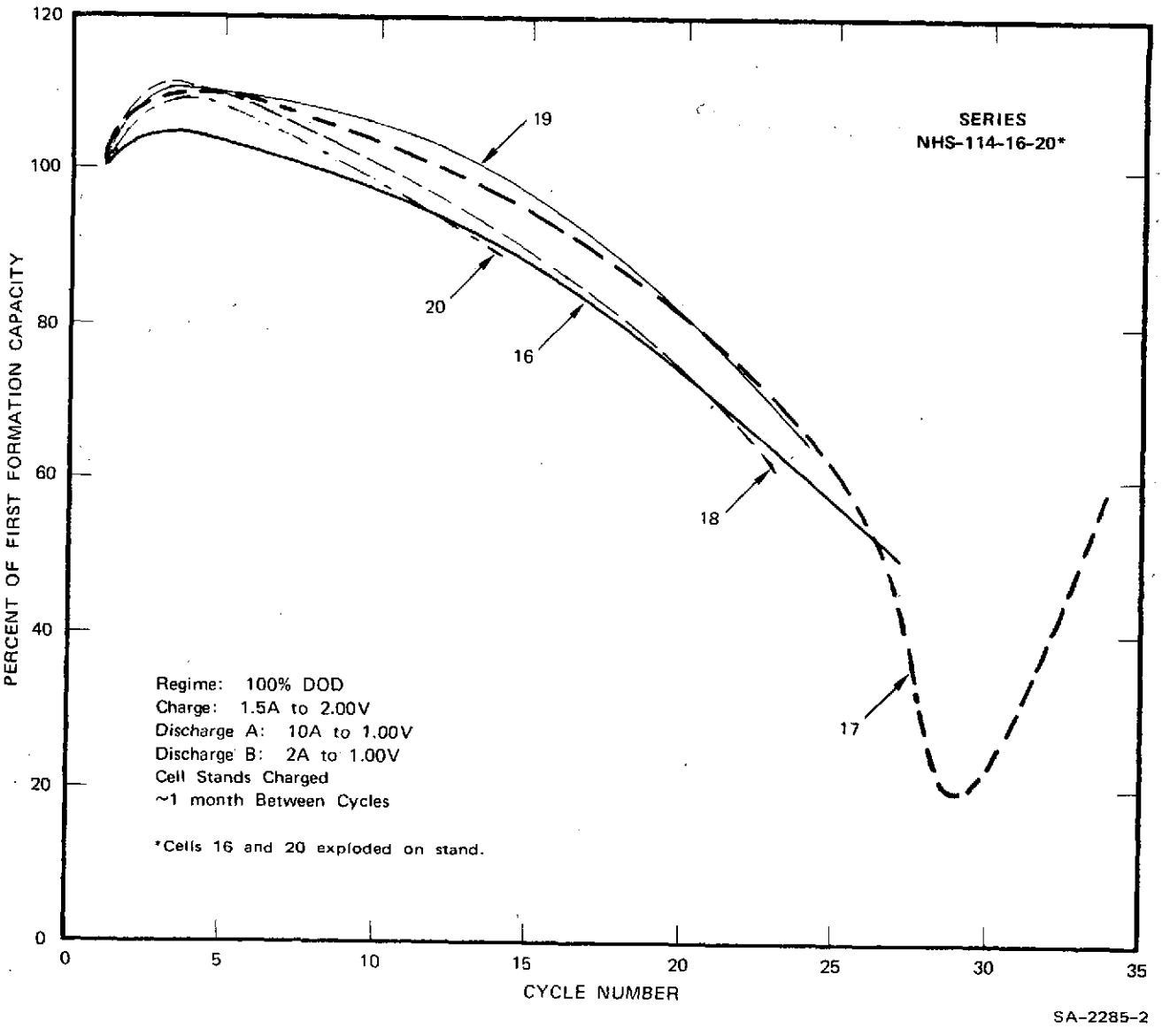

FIGURE 2 OUTPUT CAPACITY RETENTION WITH CYCLE LIFE

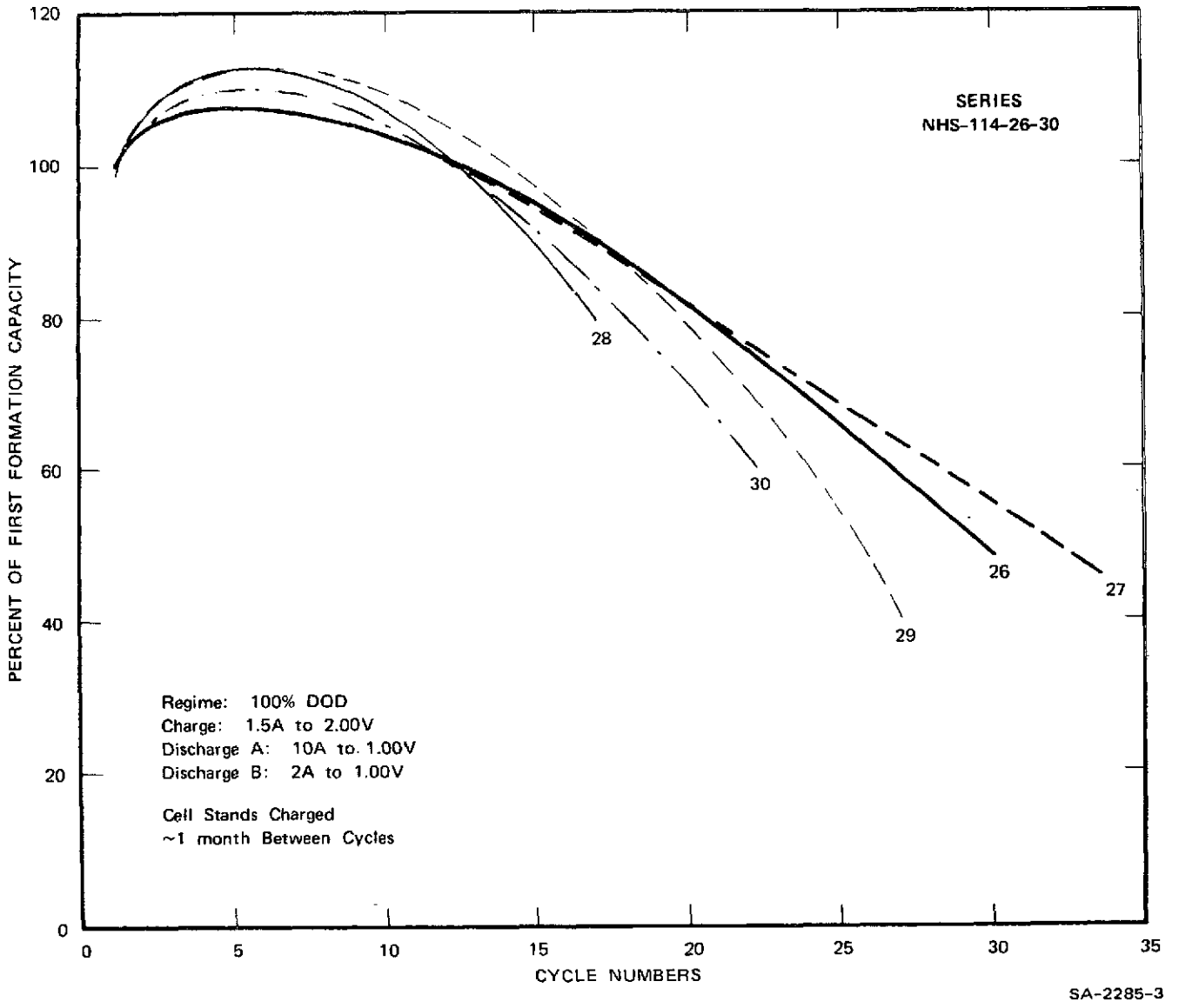

FIGURE 3 OUTPUT CAPACITY RETENTION WITH CYCLE LIFE

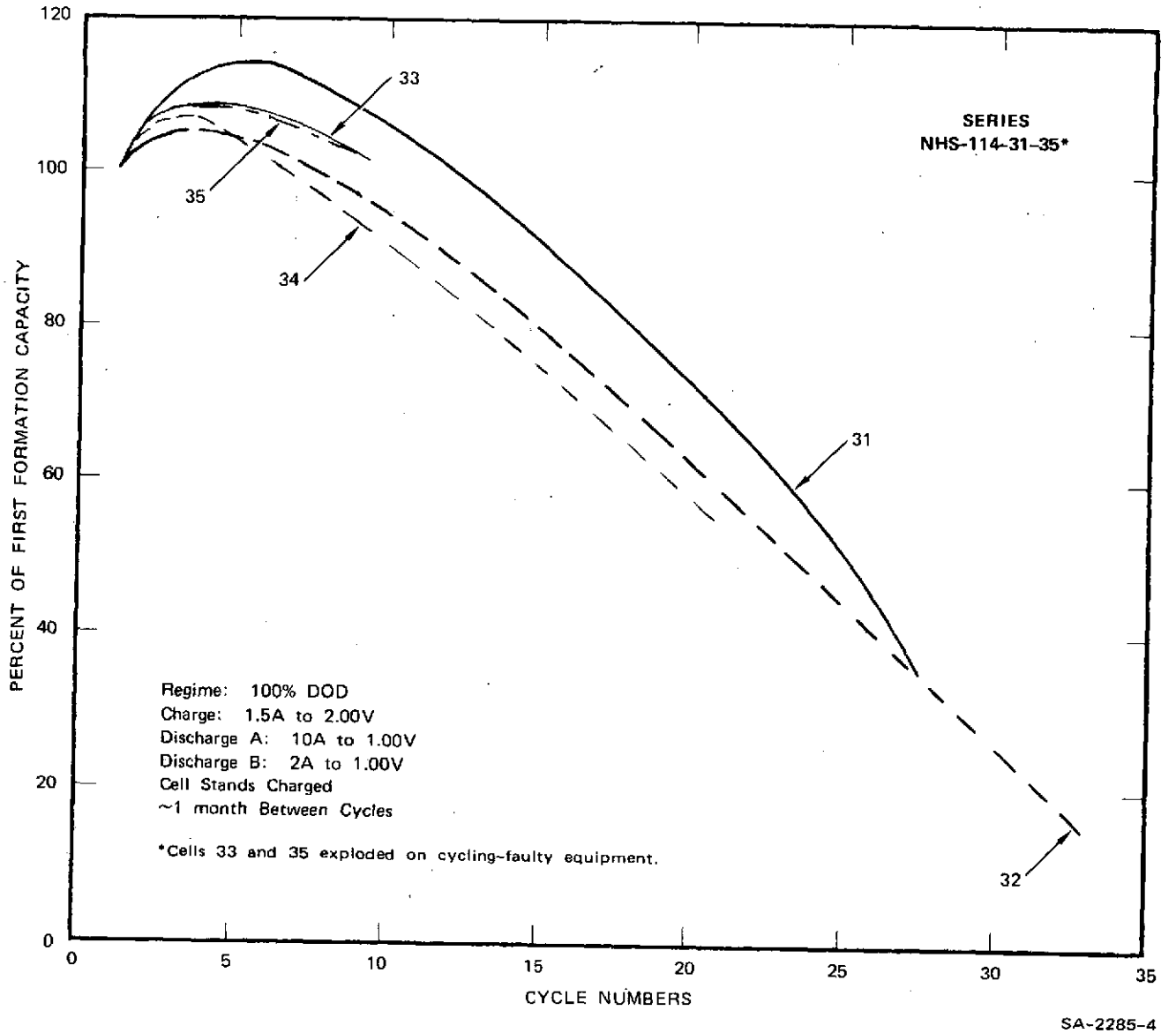

FIGURE 4 OUTPUT CAPACITY RETENTION WITH CYCLE LIFE

(3) Environmental testing does not seem to degrade wet life and cycle life of plate-locked cells.

(4) Cells with extended cure epoxy plate lock accumulated more cycles to both the 70% and 50% capacity retention levels than cells in all other subgroups.

Group of Extra Cells (Cycling Regimes: VK-1 and 100% DOD)

In this group, cell design was the major factor being tested. Several cells of varying backgrounds were collected. The designs (Reference No. 6) ranged from the early Design 2, which has only the zinc negatives bagged, to a modification of Design 5, has all electrodes bagged plus an extra separator layer between the bagged electrodes. The results obtained with this group of cycling tests are given in Table 8; the major trends are summarized as follows:

(1) As expected, cells of Design 2, which have fewer separator layers for a primary-type application, failed much earlier in cycling. The extra layer of semiflexible separator between the bagged electrodes of Design 5 appears to improve cycle life over that of cells Design 3, which have no extra layer.

(2) Although the zinc negatives of Design 5 have a lower capacity than those of Design 3, this lower capacity has not led to low capacity failures. Because of the shallow cycles of the VK-1 regime applied to these subgroups, nominally low capacity will not become a failure mode until all capacity has declined to from 10% to 15% of its original value.

(3) A comparison* of the limited data for cycling of Design 3 and Design 5 cells, using the VK-1 regime, with the data in Tables 5 and 6 suggests that a 7- to 9-month wet stand--even in the charged or float-charged conditions--does not noticeably degrade wet life and cycle life.

*Although there are differences in design, these differences are not considered large enough to invalidate a comparison in terms of parameters other than cell design.

Table 8

CYCLING RESULTS: GROUP OF EXTRA CELLS*
(Status as of 10 October 1973)

		VK-1 regime
Design 2 subgroup: total cells	2†	
No. of cells failed in cycling	2	
Average wet life (days)	646	
Average cycle life (cycles)	283	
Design 3 subgroup: total cells	5‡	
No. of cells failed in cycling	5	
Range and average of wet life (days)	996-1375[1194]	
Range and average of cycle life (cycles)	636-997 [828]	
Design 5 subgroup (VK-1): total cells	3**	
No. of cells failed in cycling	3	
Range and average of wet life (days)	1284-1319[1297]	
Range and average of cycle life (cycles)	922- 957[935]	
Design 5 subgroup (100% DOD): total cells	2	100% DOD regime
No. of cells failed in cycling		
Wet life (days)	884-1468	
Cycle life (cycles)	136- 160	
Design 7 cell (with SWRI-type GX separator): total cells	1	
No. of cells not failed in cycling	1	
Wet life (days)	1146	
Cycle life (cycles)	51	

*Cell cycling is at laboratory temperature (nominally 24°C).

†Cells HS-47-2,8 were cycled to failure at Astropower Laboratory.

‡Cells were on 7-month stand prior to cycling (2 cells on charged stand, 3 cells on float-charged stand)

**Cells were on 7 to 9 month stand prior to cycling (one cell each on charged stand, float-charged stand and discharged stand).

Failure Analysis

A detailed description of the faults and failures of these cells, and of their significance has already been published.[7] However, the faults and failures of the last 30 cells are tabulated in Table 9 of this report. Table 9 displays the incidence of the various kinds of faults. No drastic differences are evident among this group of 30 failed cells, compared to the 48 failed cells reported in Table 14 of Reference 7. The slightly higher incidence of split bags (23% vs. 19%) in the current group is probably due to the longer cycle lives and wet lives, which allows more opportunity for the bonded bag edges to weaken. The percentage of cells in the current group that failed by zinc nodule shorting is 14% vs 20% in the previous group. However, the percentage of failures in the current group by zinc-dendrite or external zinc mass shorting is 19% versus 11% in the former group. Nevertheless, the percentage of shorts by both types of zinc shorting is approximately the same in both groups. The exact mechanism that favors zinc nodule shorts over zinc dendrite shorts is not clearly established, so the differences between the two groups is unresolved.

It is difficult to distinguish low capacity per se (implying that an electrode, such as the zinc electrode, has a portion of its working material electrochemically immobilized) from electrodes that are incompletely charged because slow shorts have bypassed some of the current. Obviously, slow shorts can cause discharges to give the appearance of low capacity. One can, of course, set up individual cycling equipment for such cells, with suitable monitoring and recording of the electrical behavior, to distinguish between the two kinds of low capacity, but such extra testing was beyond the scope of this program.

The 30 cells analyzed in this program had a 3% incidence of zinc electrode slumping. However, the incidence of erosion or shedding of

Table 9

CELL FAILURE ANALYSIS: STATISTICAL BREAKDOWN OF FAULTS AND FAILURES*

Total number of cells analyzed at SRI	30
Faults	
Leaks	21
Split bags	20
Zinc nodule shorts (confirmed)	12
Zinc dendrite shorts (probable)	17
Low capacity	1
Zinc electrode slumping	3
Zinc electrode erosion	14
Total Faults	88
Physical and (or) Formal Causes of Cell Failure	
Zinc nodule short	12
Zinc dendrite or filament short	17
Nominally low capacity	1
Total Failures	30

*For cells failed between 31 October 1972 and 10 October 1973.

working material from the zinc electrodes in the current group was equal to 16%. This erosion and shedding is probably associated with the longer cycle life and wet life, which gave more opportunity for redistributing the zinc-containing material that existed outside of the bags. The details of the failure analysis of the 30 cells are given for each category, group and subgroup in Tables 10 to 16.

Failure Modes: Breakdown by Cell Test Group

The overall failure statistics in Tables 10 to 16 indicate that zinc nodule and dendrite (filament) shorting together accounted for nearly all failures in each cell test group. However, there were sufficient systematic differences in the fault and failure patterns of cells from different groups to warrant a breakdown of failure analysis findings. This breakdown by cell test group is also shown in Tables 10 through 16. The major findings from the analysis, which are similar to those cited in Reference 7, can be summarized as follows:

(1) Zinc nodule shorts were the dominant failure mode of cells subjected to 100% DOD with charged stand between periodic discharges. This failure mode is also dominant for Viking cells of the charged and float-charged stand subgroups that failed during stand or early in subsequent cycling, and for the temperature-battery/cell group. Inasmuch as several more cells from other groups failed early in life by this mode, failure analysis has established zinc nodule shorts as the major cause for cell failures in long cycling. Zinc nodule shorts were not observed in the few failed cells from the Viking discharged-stand category, but were observed in Viking cells that were placed on cycling immediately after being activated.

(2) Shorts associated with the presence of dentritic and mossy zinc (and ascribed to zinc filament penetration) are the dominant failure mode for those cells from the Viking and other groups that attained at least several hundred cycles on the VK-1 and VK-2 regimes.

Table 10

CELL FAILURE ANALYSIS, 3-PLATE PILOT CELL
(Status as of 10 October 1973)

Cell No.	Cycle Life	Wet Life(d)	Leaks	Bag Splits	Slumping	Erosion	Failure Notations
HS-16-12	777	1230	+*	+	-	+	Probable shorting through both Zn dendrites, and through the large mass of Zn bridging the splits in both Zn and Ag bags.

*Inadequate RTV rubber seal.

Table 11

VIKING,* FLOAT-CHARGED STAND CATEGORY
(Status as of 10 October 1973)

Cell No.	Stand Temp. °C	Cycle Life	Wet Life(d)	Leaks	Bag Splits	Slumping	Erosion	Failure Notations
HS-59-24	24†	810	1222	+	-	-	-	A Zn shorting nodule was found

*Cycled on the VK-2 regime

†Float-charged stand for 24 months prior to cycling.

Table 12

VIKING,* DISCHARGED WET-STAND CATEGORY
(Status as of 10 October 1973)

Cell No.	Stand Temp. °C	Cycle Life	Wet Life(d)	Bag Leaks	Bag Splits	Bag Slumping	Bag Erosion	Failure Notations
HS-59-30	24†	1447	1507	+	+	-	-	Shorting through large Zn mass bridging splits in both Zn and Ag bags.
HS-90-1	24††	1163	1237	-	+	-	-	Shorting through numerous Zn dendrites.

*Cycling on the VK-2 regime.

†On discharged-stand for 25 months prior to cycling.

††On discharged-stand for 21 months prior to cycling.

Table 13

VIKING,* CONTINUOUS CYCLING IMMEDIATELY AFTER ACTIVATION
(Status as of 10 October 1973)

Cell No.	Cycle Life	Wet Life(d)	Bag Leaks	Bag Splits	Bag Slumping	Bag Erosion	Failure Notations
HS-86-1	2156	1218	+	+	-	-	A Zn shorting nodule was found.
HS-86-2	2004	1142	+	+	-	-	3 Zn shorting nodules were found.

*Cycled on the VK-2 regime.

Table 14

CELL FAILURE ANALYSIS, TEMPERATURE-BATTERY/CELL GROUP
(Status as of 10 October 1973)

Cell No.	Temp. °C	Cycle Life	Wet Life(d)	Bag Leaks	Bag Splits	Slumping	Erosion	Failure Notations
HS-61-11	10*	1226	1369	+	+	-	-	A small Zn shorting nodule was found. Shorting also probably occurred through the massive Zn deposits bridging the Zn and Ag bag splits.
HS-82-4	32†	1019	1188	-	+	-	+	Probable Zn dendrite shorts.

*Cycled singly.

†Cycled in a battery.

Table 15

CELL FAILURE ANALYSIS, PLATE LOCK CELL GROUP
100% DOD Regime*
(Status as of 10 October 1973)

Cell No.	Cycle Life	Wet Life(d)	Bag Leaks	Bag Splits	Slumping	Erosion	Failure Notations
NHS-114-0	3	1050	+†	-	-	-	Gradual self-discharge of Zn plates
NHS-114-3	27	925	-	-	-	-	Probable Zn dendrite short
NHS-114-4	27	925	+	-	-	-	Probable Zn dendrite short
NHS-114-16	27	923	-	+	-	-	A shorting Zn nodule was found (Cell exploded)
NHS-114-18	24	837	+	+	-	-	A shorting Zn nodule was found
NHS-114-19	22	793	+	-	-	+	A shorting Zn nodule was found
NHS-114-26	31	1013	-	+	-	+	A shorting Zn nodule was found
NHS-114-29	26	914	-	-	-	-	Probable Zn dendrite short. The remains of a large decomposed dendrite was found.
NHS-114-30	22	789	+	-	-	-	A shorting Zn nodule was found
NHS-114-31	28	929	+	-	-	+	A shorting Zn nodule was found
NHS-114-32	33	1069	-	-	-	+	Probable Zn dendrite short
NHS-114-33	10	417	-	+	-	-	Cell exploded because of cycling equipment failure.

*Except NHS-114-0 which remained on continuous charged stand after the 3 formation cycles. All others were on approximately one month charged stand between cycles.

†Inadequate RTV rubber seal.

Table 16

CELL FAILURE ANALYSIS, DESIGN VARIATION AND EXTRA CELL GROUPS
(Status as of 10 October 1973)

Cell No.	Design No.	Regime	Cycle Life	Wet Life(d)	Leaks	Bag Splits	Slumping	Erosion	Failure Notations
HS-51-4	3	VK-1*	997	1342	+	+	-	+	A shorting Zn nodule was found
HS-51-7	3	VK-1*	(971) 1248	(1375)† 1667	-	+	-	+	Probable Zn dendrite shorts
HS-54-2	5	VK-1*	922	1284	+	+	-	+	Probable Zn dendrite shorts, and possible minute nodule(s) short
HS-54-5	5	100% DOD*	160	1468	+	-	-	+	Probable Zn dendrite shorts, and low capacity
HS-54-7	5	VK-1*	(925) 1104	(1288) 1470	+	+	-	+	Probable Zn dendrite shorts
HS-66-1	7	VK-1	724	985	+	+	-	-	Shorting through Zn mass bridging Zn and Ag bag splits
HS-66-3	7	VK-1	1127	1388	+	+	+	+	Shorting through Zn mass bridging Zn and Ag bag splits
HS-66-5	7	VK-1	(851) 1164	(1112) 1428	+	+	+	+	Shorting through Zn mass bridging Zn and Ag bag splits
HS-66-10	6	VK-1	1109	1316	+	+	+	+	A shorting Zn nodule was found
HS-66-11	8	VK-1	892	1141	+	+	-	-	A shorting Zn nodule was found.

*Cycled singly; all others cycled in a battery.

†Numbers in ( ) indicate cycle number or wet life in days at time of first failure (cell was allowed to continue cycling). The other number refers to cycle number or wet life in days at conclusion of cycling.

(3) Nominally low cell capacity depends on the criteria applied in defining it. One cell was judged to have failed in this mode because it delivered only approximately 20% of its nominal rated capacity. Presumably, such a cell would not be used when it reaches such a low capacity. All cells seem to decline in capacity after the first several cycles, and the usefulness of a cell, if it does not fail in some other mode, depends on the delivery of a pre-established minimum capacity. Accordingly, the initial capacity is made high enough to accommodate the decline in capacity over the cycle span desired. The shallow cycling regimes VK-1 and VK-2 allow a long cycle life of cells having large initial capacities, as compared to short cycle life at the deep depths of discharge in other cells of similar initial capacity.

(4) Bag splits were common in all cell groups, except those in the Viking charged stand, in the float-charged stand categories, and infrequently in the plate-lock cell subgroup cycled on 100% DOD. There may be a correlation between bag splits (especially when both Zn and Ag bags are split) and failure by shorting through the mass of Zn external to the bags.

(5) All cells with lids sealed only with RTV silicone adhesive, developed leaks. A substantial percentage of the cells in all other groups also leaked, but no direct correlation is apparent between cell leakage and a particular failure mode.

(6) About one-half of all cells showed zinc electrode erosion. About 57% of these cells and all cells showing electrode slumping were from batteries and cells from the Design Variation and Extra Cell groups. All three instances of slumping originated in cells operated in a battery in the design variation group.

Test Results on Cells Made at SRI

Two test series of cells were made at SRI. Electrodes were supplied by a vendor that made them according to NASA specifications (similar or identical to the electrodes used in the cells made at MDC).

The cell cases and lids (electrode posts already attached to the lids) were supplied from NASA stock. SRI fabricated the separators and added electrolyte and other minor components necessary to complete the cells.

Each series comprised 12 test cells, grouped by threes as shown in Table 17. Each group represents a particular separator composition. Graphs of percent of formation capacity versus number of cycles display the decline in capacity. These graphs are shown as Figures 5 to 8 for the first series and as Figures 9 to 12 for the second series. The performance of each cell in a group and the group average are plotted in each graph. One may conceive of an envelope of curves or a band that would define each group average curve. Table 17 lists the group average numbers obtained for both test series.* The differences between the two series appears to be quite substantial, and these differences may be explained, at least in part, in the history of the cells.

Testing of the First Series of Cells

The formation cycles for the first series of cells was performed on a five-station charge-discharge panel, having an electromechanical cutoff meter as the limit control for the 2.005V discharge limit and the 1.000V discharge limit. Earlier experience in cycling the MDC (NHS-114 group in Table 7) cells indicated that a few millivolts difference in the set value could make a significant difference in the input or output. The meter was always set correctly according to a reference standard. However, vibrations of the floor or building triggered the meter to cutoff at an equivalent of a few to several millivolts before the set point. Variations in observed capacities

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* Specific cycle performances appear in Tables 20 and 21 and are derived from Figures 5 - 8 and 9 - 12.

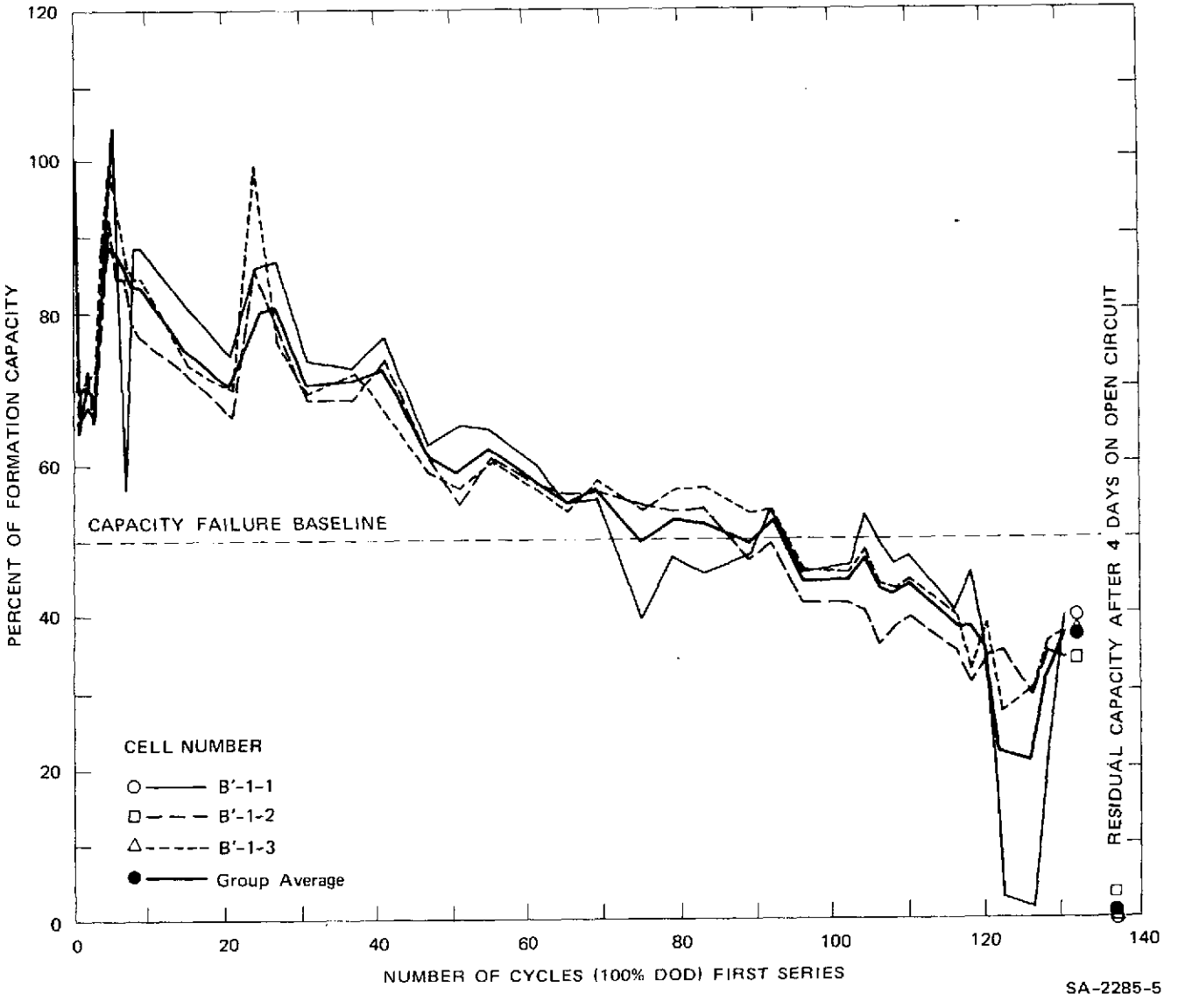

FIGURE 5 CAPACITY CHANGE WITH CYCLING

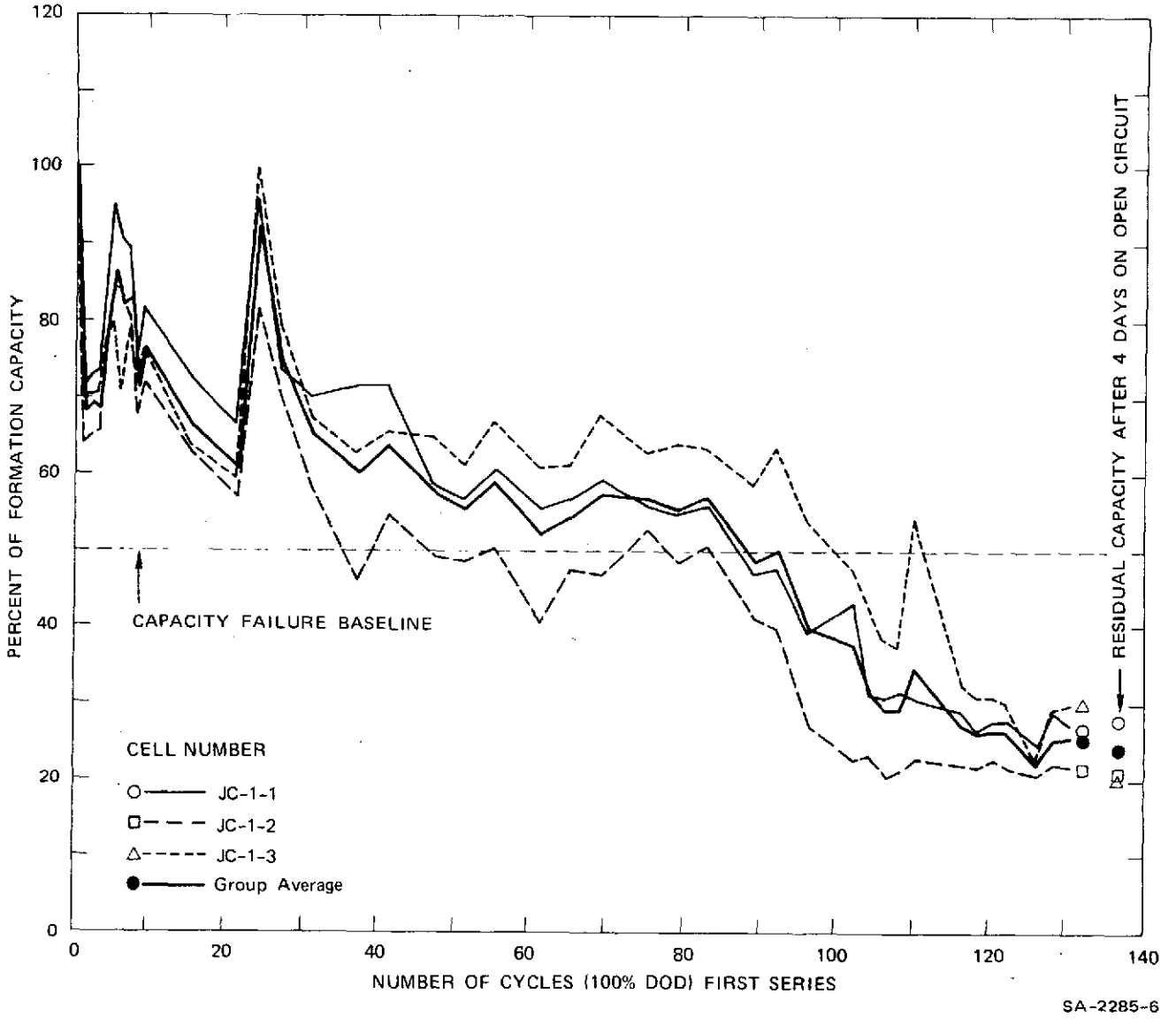

FIGURE 6 CAPACITY CHANGE WITH CYCLING

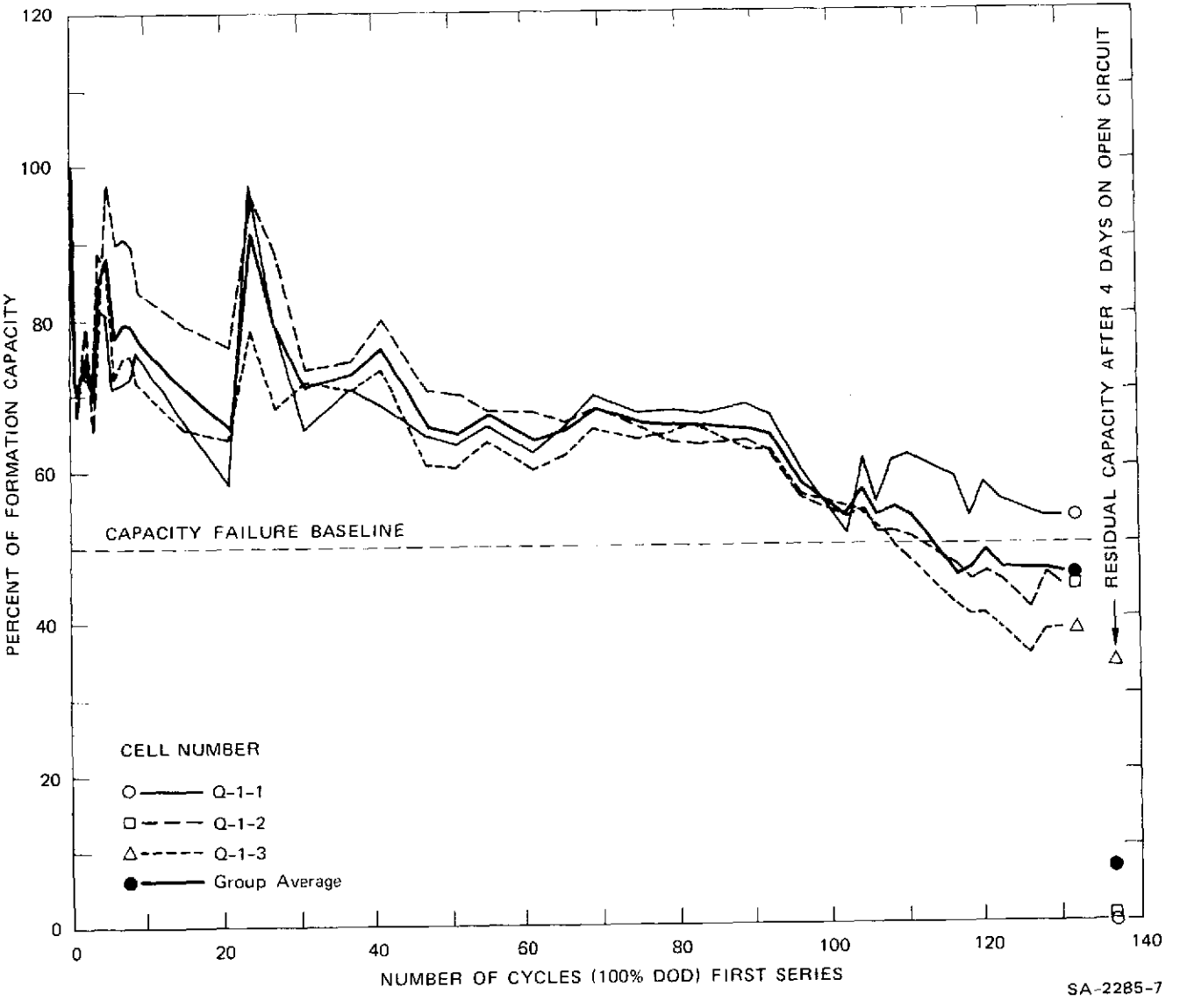

FIGURE 7 CAPACITY CHANGE WITH CYCLING

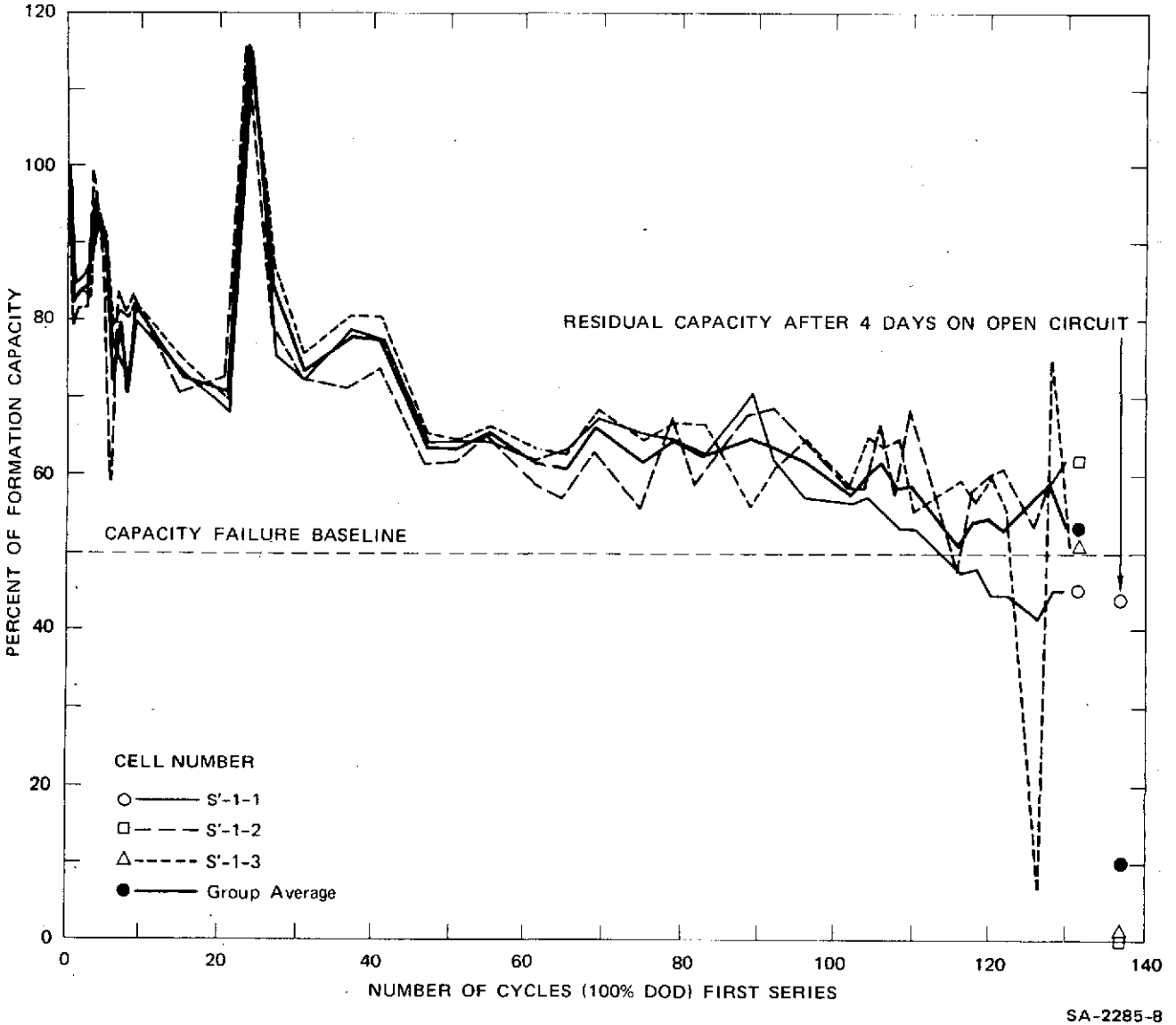

FIGURE 8 CAPACITY CHANGE WITH CYCLING

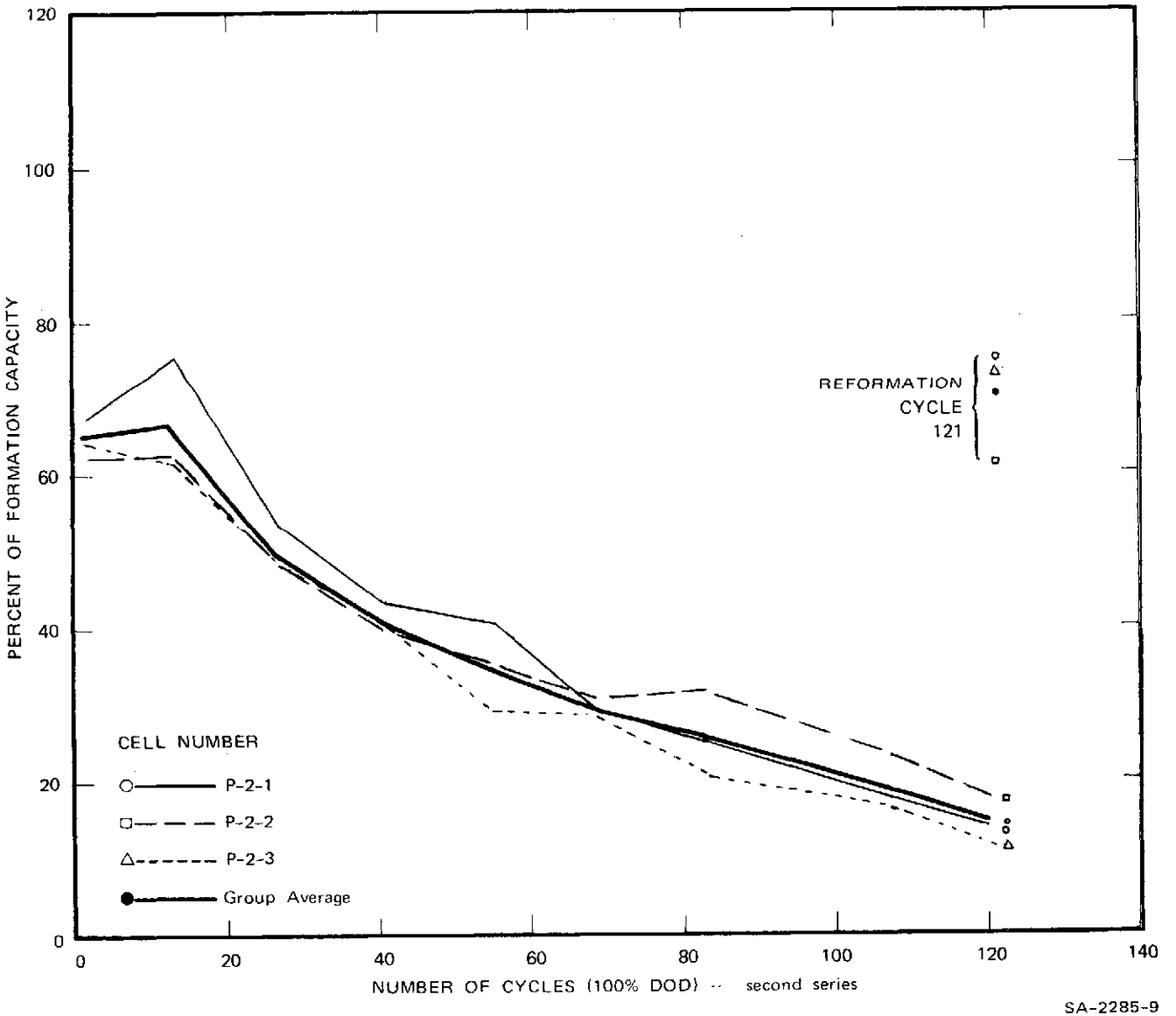

FIGURE 9 CAPACITY CHANGE WITH CYCLING

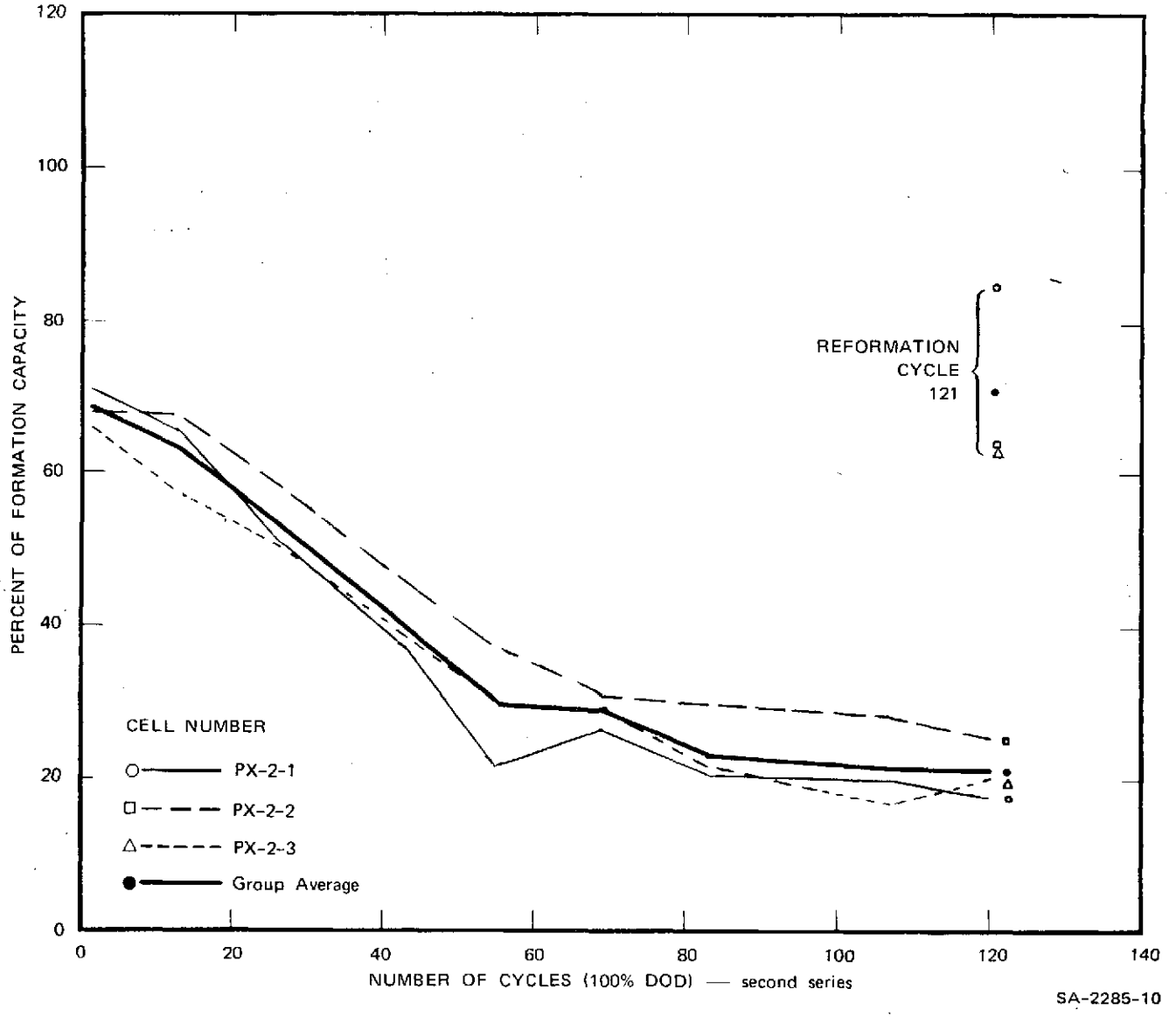

FIGURE 10 CAPACITY CHANGE WITH CYCLING

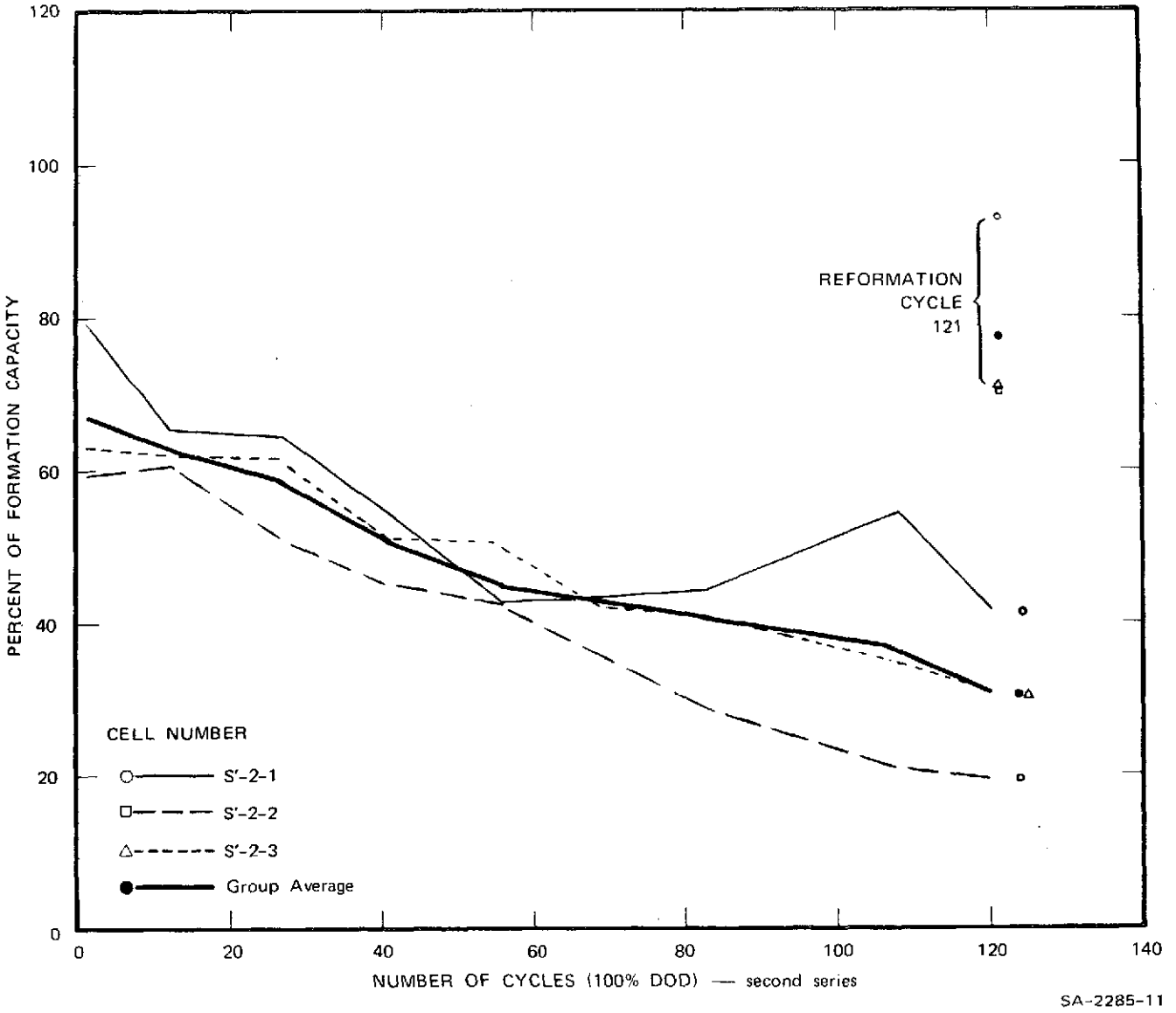

FIGURE 11 CAPACITY CHANGE WITH CYCLING

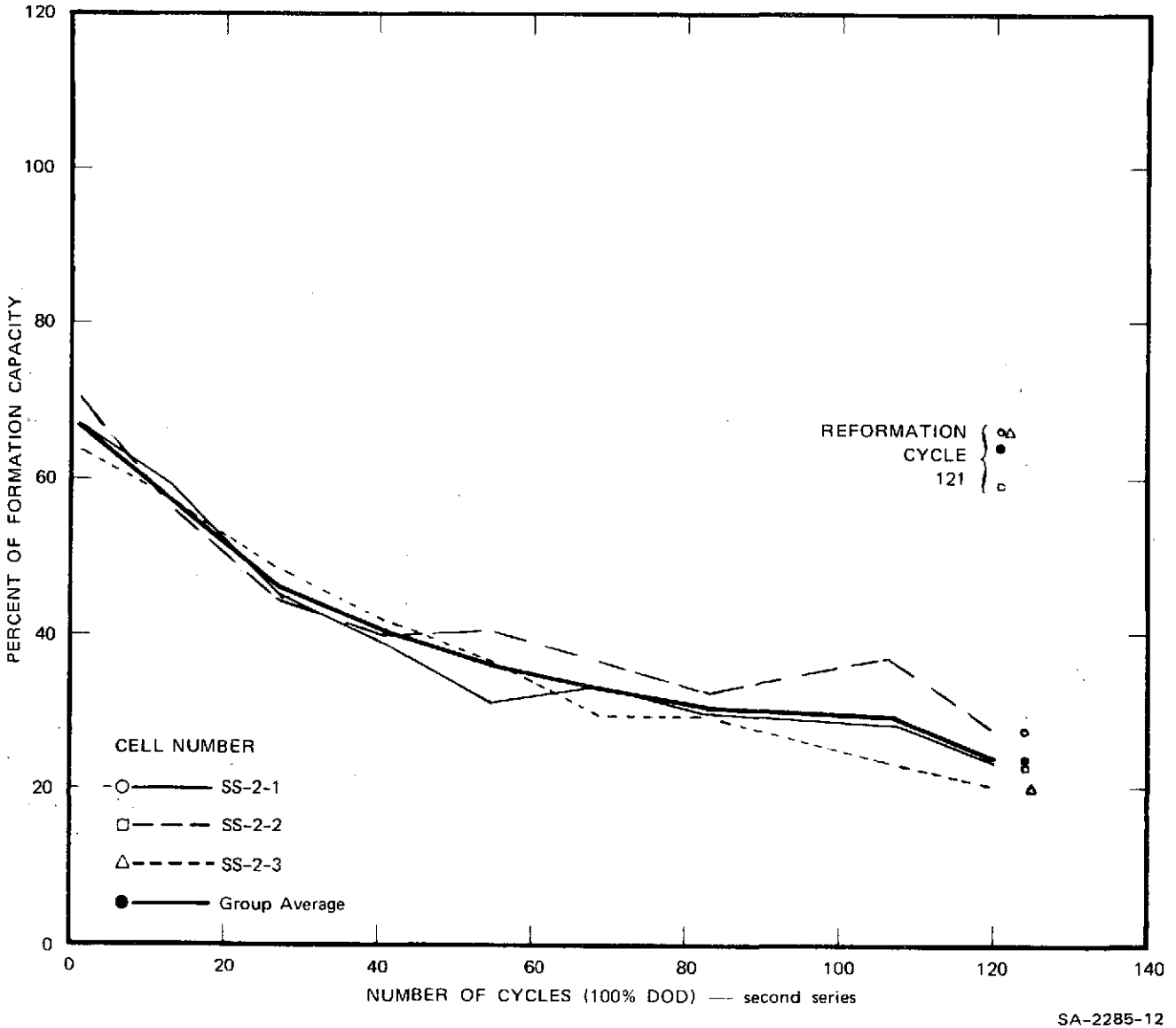

FIGURE 12 CAPACITY CHANGE WITH CYCLING

Table 17

GROUP AVERAGE* CYCLE LIFE
TO 50% OF FORMATION CAPACITY

Cell Numbers	Separator	Band Width Cycles
	First Series	
B´-1-1 B´-1-2 B´-1-3	B´	80-94
JC-1-1 JC-1-2 JC-1-3	JC	86-93
Q-1-1 Q-1-2 Q-1-3	Q	109-116
S´-1-1 S´-1-2 S´-1-3	S´	†
	Second Series	
P-2-1 P-2-2 P-2-3	P	25-29
PX-2-1 PX-2-2 PX-2-3	P	27-32
S´-2-1 S´-2-2 S´-2-3	S´	42-47
SS-2-1 SS-2-2 SS-2-3	SS	21-27

*Determined by overlaying a band 4-6 mm wide on Figures 5-8 and 9-12, to generate a band curve (smooth rather than articulated). Intersection with the 50% capacity line yielded the numbers given.

†Did not drop to or below 50% capacity.

can easily be attributed to this cause. Capacities observed in the third formation were employed as values of nominal capacity for each cell.

Regular and automatic life cycling using a 2-cycle per day 100% DOD regime was started using the cell capacity data acquired during formation. Records of charge and discharge capacity were maintained; it was from these records that the curves in Figures 5 to 8 were constructed. Records for Cycles 15, 41, and 120 are presented in Tables 18a, 18b, and 18c.

In the first series to Cycle 130, it is to be noted that the group average for the S′ separator stayed above the 50% capacity level. Clearly, it was the best separator, confirming the findings of the selection process on the preceeding contract (NAS 3-15686). A subsequent four-day stand charged on open circuit disclosed that 7 of the 12 cells had slow shorts (See Figures 5-8) as shown by the plots of the last data points in the graphs. Only a few more cycles were applied after the stand period, many of the cells recovering somewhat from the slow shorts. However, at this point even the S′-group of cells had a group average below 50% (one S′-cell yielded 67%). It was decided to stop cycling and dismantle the cells for failure analysis.

Testing of the Second Series of Cells

The formation charges for the second series were provided by the 17-station automatic cycling panel, with the voltage limit for the first formation set at 2.005 V. Because the capacity inputs were lower than desired, the second formation charge voltage limit was set at 2.050 V, per agreement with NASA. After the discharge capacity was determined for the

Table 18a

100% DOD CYCLE TESTS
First Series for Cycle 15
On 18 May 1974

Separator	Cell No.	Formation Capacity	Discharge Time (hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
B′	B′-1-1	5.6	1.85	4.53	80.5	74.7
	B′-1-2	5.7	1.67	4.08	72.1	
	B′-1-3	5.2	1.55	3.80	74.5	
JC	JC-1-1	5.3	1.55	3.80	73.1	66.7
	JC 1-2	5.7	1.45	3.55	63.4	
	JC-1-3	5.2	1.35	3.31	63.7	
Q	Q-1-1	5.2	1.42	3.48	66.8	70.7
	Q-1-2	5.4	1.75	4.29	79.4	
	Q-1-3	5.1	1.38	3.38	65.9	
S′	S′-1-1	4.4	1.30	3.19	73.2	72.9
	S′-1-2	4.6	1.32	3.23	70.4	
	S′-1-3	4.5	1.37	3.36	75.2	

Average Discharge Current: 2.45A.

Table 18b

100% DOD CYCLE TESTS
First Series for Cycle 41
On 1 June 1973

Separator	Cell No.	Formation Capacity	Discharge Time (hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
B′	B′-1-1	5.6	1.78	4.31	76.6	72.1
	B′-1-2	5.7	1.72	4.15	73.4	
	B′-1-3	5.2	1.42	3.43	66.3	
JC	JC-1-1	5.3	1.55	3.75	71.2	63.6
	JC-1-2	5.7	1.28	3.10	54.5	
	JC-1-3	5.2	1.40	3.39	65.1	
Q	Q-1-1	5.2	1.47	3.55	68.1	75.5
	Q-1-2	5.4	1.78	4.31	79.9	
	Q-1-3	5.1	1.55	3.76	73.3	
S′	S′-1-1	4.4	1.40	3.39	77.7	77.3
	S′-1-2	4.6	1.40	3.39	73.8	
	S′-1-3	4.5	1.48	3.59	80.3	

Average Discharge Current: 2.42A

Table 18c

100% DOD CYCLE TESTS
First Series for Cycle 120
On 11 July 1973

Separator	Cell No.	Formation Capacity	Discharge Time (hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
B′	B′-1-1	5.6	0.83	2.00	35.5	36.5
	B′-1-2	5.7	0.83	2.00	35.3	
	B′-1-3	5.2	0.83	2.00	38.7	
JC	JC-1-1	5.3	0.60	1.44	27.3	26.8
	JC-1-2	5.7	0.53	1.28	22.5	
	JC-1-3	5.2	0.67	1.60	30.7	
Q	Q-1-1	5.2	1.25	3.01	57.8	48.3
	Q-1-2	5.4	1.05	2.52	46.7	
	Q-1-3	5.1	0.87	2.08	40.5	
S′	S′-1-1	4.4	0.82	1.96	44.9	54.6
	S′-1-2	4.6	1.13	2.72	59.2	
	S′-1-3	4.5	1.12	2.67	59.7	

Average Discharge Current: 2.40A.

second formation cycle, the normal 100% DOD cycling of the cells was started. In this series of tests the electromechanical cutoff meter relay used in the first series of tests was replaced by an electronic device not sensitive to mechanical motion. Variations in observed capacities therefore must be attributed to causes other than variations in performance of the charging curcuitry.

The capacities observed in formation charging and the performance data for regular 100% DOD life-cycling are presented in Tables 19a, 19b, and 19c. These tables present the numerical data taken at Cycles 13, 41, and 120 in the testing of the second series. Data such as these were used to plot the curves of Figures 9 through 12.

Comparison of Series I and Series II Cell Tests

The formation capacities of the first series of tests are lower than the second series. The charge voltage limit in the first series was set at 2.005 volts and was increased to 2.050 volts in the second series of tests.

The discharge current was 2.7 A for the second series as compared to from 2.4 to 2.5 A for the first series, and therefore the discharge times in the second test series were shorter. This shorter discharge time produces a smaller number of cycles to the 50% point (i.e., a capacity return of 50% of the formation capacity). A comparison of the data for Cycle 41 for both series (Tables 18 and 19) clearly shows the effects of the higher discharge current for the second series. No other extraordinary effects were noted during cycling.

Table 19a

100% DOD CYCLE TESTS
Second Series for Cycle 13
On 24 October 1973

Separator	Cell No.	Formation Capacity	Discharge Time (hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
P	P-2-1	5.9	1.60	4.45	75.7	66.8
	P-2-2	6.6	1.48	4.12	62.7	
	P-2-3	6.2	1.38	3.85	62.1	
P	PX-2-1	5.7	1.33	3.71	65.4	63.5
	PX-2-2	5.3	1.28	3.57	67.8	
	PX-2-3	6.3	1.30	3.61	57.3	
S′	S′-2-1	4.3	1.02	2.83	65.3	62.6
	S′-2-2	6.7	1.45	4.03	60.6	
	S′-2-3	5.6	1.25	3.48	61.8	
SS	SS-2-1	6.1	1.30	3.61	59.0	57.6
	SS-2-2	6.3	1.27	3.52	56.4	
	SS-2-3	6.4	1.32	3.66	57.5	

Average Discharge Current: 2.78A

Table 19b

100% DOD CYCLE TESTS
Second Series for Cycle 41
On 7 November 1973

Separator	Cell No.	Formation Capacity	Discharge Time (Hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
P	P-2-1	5.9	0.93	2.53	43.0	40.5
	P-2-2	6.6	0.93	2.53	38.5	
	P-2-3	6.2	0.92	2.49	40.2	
P	PX-2-1	5.7	0.80	2.17	38.2	41.9
	PX-2-2	5.3	0.92	2.49	47.2	
	PX-2-3	6.3	0.93	2.53	40.1	
S′	S′-2-1	4.3	0.88	2.39	55.3	50.3
	S′-2-2	6.7	1.10	2.98	44.8	
	S′-2-3	5.6	1.05	2.85	50.6	
SS	SS-2-1	6.1	0.87	2.35	38.3	40.0
	SS-2-2	6.3	0.92	2.49	39.8	
	SS-2-3	6.4	0.98	2.66	41.8	

Average Discharge Current: 2.71A.

Table 19c

100% DOD CYCLE TESTS
Second Series for Cycle 120
On 18 December 1973

Separator	Cell No.	Formation Capacity	Discharge Time (Hr)	Ampere Hrs	Percent of Formation Capacity	Group Average Percent
P	P-2-1	5.9	0.37	0.83	14.1	14.4
	P-2-2	6.6	0.52	1.16	17.7	
	P-2-3	6.2	0.28	0.70	11.3	
P	PX-2-1	5.7	0.40	1.10	17.6	20.9
	PX-2-2	5.3	0.50	1.31	24.9	
	PX-2-3	6.3	0.57	1.27	20.1	
S′	S′-2-1	4.3	0.62	1.81	41.9	30.6
	S′-2-2	6.7	0.48	1.26	18.9	
	S′-2-3	5.6	0.67	1.75	31.1	
SS	SS-2-1	6.1	0.50	1.43	23.3	24.0
	SS-2-2	6.3	0.67	1.75	28.0	
	SS-2-3	6.4	0.50	1.31	20.6	

Average Discharge Current: 2.55A.

Failure Analysis

Cells from both series were carefully taken apart, and all parts examined. Certain characteristics common to both series were noted, such as the total absence of seam splits or coating cracks, and the frequent occurrence of zinc dendrite deposition on the back side of the bags containing the silver electrodes (case wall side).

An interesting finding of the failure analysis for the first series was the presence of very small nodules (described as nailhead nodules) on the back faces of all but one of the Zn bags, and all but three of the Ag bags. The quantities varied from a few to several hundred. The failure analysis data appear in Table 20. Judging from the patterns of the small nodules, it is suspected that they were covered over by a very thin layer of leafy dendritic zinc, which was dissolved by the time disassembly took place. These structures, possibly acting as slow shorts shunting a part of the current, could account for the apparent decline in cell capacity. Similar nailhead nodule penetrations were noted in the working faces of the separator bags. Separators made from B′ and Q materials had a higher density of nodules than the separator made from S′-type materials.

Some slumping was observed in all zinc plates. The Q group exhibited the most slumping, while the B′ and S′ groups showed the least amount of slumping. Only a few instances of zinc plate erosion or shedding were found; the most severe erosion was observed on a plate from a cell in the Q group.

Very little silver was found in the zinc bags due to time span of cell testing. The results of silver analyses are shown in Table 21.

As shown in Table 22, one significant difference in the second series of cells compared to the first series, was that no nodules or dendrites were found on the back of the zinc bags. This may have been

Table 20
FAILURE ANALYSIS OF TWO-PLATE CELLS
First Series

Cell No.	3d Form. Capacity Ahr	Final Capacity Cycle 130 Ahr	Specific Cycle Life to 50% Capacity Days	Zn Nodule Penetration Back of Zn Bag	Zn Nodule Penetration Back of Ag Bag	Zn Nodule Penetration Active Face Zn Bag	Zn Nodule Penetration Active Face Ag Bag	Separator Erosion or Damage	Slumping	Plate Erosion
B'-1-1	5.63	2.22	71	+++++[a]	++	+	+	No	x[b]	slight
B'-1-2	5.66	1.94	87	+++++	++	++++	+++++	Yes (Zn) 3 cm^2	x	No
B'-1-3	5.17	1.94	94	+++++	++	++++	++++	No	x	No
JC-1-1	5.27	1.43	87	+++++	-	+++++	+	Yes (Ag)	xxx	No
JC-1-2	5.69	1.23	35	+++	+	++	++	No	xx	No
JC-1-3	5.20	1.51	100	+++	++	-	-	No	x	No
Q-1-1	5.21	2.78	134	+++++	-	++++	+++++	Yes	xxxx	Very significant
Q-1-2	5.40	2.42	112	+++++	+++++	+++	+++++	No	xxxx	Slight
Q-1-3	5.13	1.98	98	+++++	+++	++	++	No	xxx	No
S'-1-1	4.36	1.98	114	++	+++	++	-	No	x	No
S'-1-2	4.59	2.82	134	-	-	+	+	No	x	No
S'-1-3	4.47	2.26	134	+++++	++	+++++	+	No	x	No

[a] Numerous (hundreds of small "nailhead nodules") ≡ +++++, > a few ≡ +, > none ≡ - .

[b] Considerable ≡ xxxx, > moderate ≡ xxx, > light ≡ xx, > slight ≡ x, > none ≡ - .

There were no seam splits or coating cracks in any of the bags.

Table 21

SILVER CONTENT OF SEPARATORS*

First Series of Cells			Second Series of Cells		
Cell No.	Silver Bag Weight † Mg/cm^2	Zinc Bag Weight † Mg/cm^2	Cell No.	Silver Bag Weight † Mg/cm^2	Zinc Bag Weight † Mg/cm^2
B'-1-1	8.0	0.3	P-2-1	2.9	0.2
B'-1-2	6.1	0.2	P-2-2	2.4	0.1
B'-1-3	7.3	0.1	P-2-3	2.3	0.1
JC-1-1	6.8	0.2	PX-2-1	1.9	0.1
JC-1-2	4.1	0.0 +	PX-2-2	1.8	0.1
JC-1-3	7.4	0.1	PX-2-3	1.9	0.1
Q-1-1	8.2	0.2	S-2-1	2.5	0.1
Q-1-2	7.6	0.0 +	S-2-2	1.9	0.1
Q-1-3	9.2	0.3	S-2-3	2.1	0.1
S'-1-1	7.0	0.3	SS-2-1	1.9	0.2
S'-1-2	7.1	0.0 +	SS-2-2	2.1	0.1
S'-1-3	9.2	0.2	SS-2-3	2.2	0.1
Pilot	4.7	0.1			

*Samples were cut from the working faces.

†Average of two determinations.

Table 22

FAILURE ANALYSIS OF TWO-PLATE CELLS
Second Series

Cell No.	2nd Form. Capacity Ahr	Final Capacity Cycle 120 Ahr	Specific Cycle Life to 50% Capacity Days	Zn Nodule or Dendrites Back of Zn Bag	Zn Nodule* or Dendrites Back of Ag Bag	Zn Nodule* or Dendrites Active Face of Zn Bag	Zn Nodule* or Dendrites Active Face of Ag Bag	Separator Erosion or Damage**	Slumping	Plate Erosion
P-2-1	5.88	0.83	32	-	++†	++†	+†	No	-	-
P-2-2	6.57	1.16	26	-	+++	++	+	-	-	-
P-2-3	6.19	0.70	26	-	++	++	+	No	-	-
PY-2-1	5.67	1.00	28	-	+++++	+	+	No	-	-
PY-2-2	5.26	1.31	37	-	+++++	+	+	No	-	-
PY-2-3	6.31	1.27	27	-	+++++	+	+	No	-	-
S'-2-1	4.33	1.81	47	-	+++++	-	-	No	-	-
S'-2-2	6.65	1.26	57	-	++	-	-	No	-	-
S'-2-3	5.62	1.75	30	-	+++++	++	++	No	-	-
SS-2-1	6.13	1.43	23	-	-	-	-	No	-	-
SS-2-2	6.25	1.75	22	-	-	-	-	No	-	-
SS-2-3	6.37	1.31	26	-	-	-	-	No	-	-

*No indication is made here that penetration did or did not occur.

**There were no bag seam splits on any COHS

†Numerous Zn masses $\geq \sim$ 60% of area = +++++, $>$ 1% $\equiv$ +, none = -

influenced by the fact that these cells were analyzed in the discharged state. Except for cells having the SS separator, all cells had substantial amounts of flat dendritic zinc deposits on the backs of the Ag separator bags. These deposits had at times been connected electronically with the zinc mush deposits that filled the V-notch groove at the edges (bottom) of the two separator bags in each cell.

The SS cells had no dendritic zinc deposits on or between the working faces. Two of the S´ cells, likewise, did not have such deposits on or between the working faces. The other cells had small amounts of these deposits on about 1% of the face areas. There was no erosion or spalling of the separator coatings anywhere in any of the cells. Furthermore, there was no obvious slumping or plate shedding or erosion. However, in most if not all the cases, the central areas of the negative plates were somewhat densified (this was true in the first series also). One could postulate that this phenomenon might precede ultimate slumping.

DISCUSSION

The large fluctuations of the small-number statistics governing the results of this test program introduce considerable uncertainties, especially in a more detailed analysis. However, the test program has provided worthwhile answers to the most important questions pursued.

The major objective of the silver-zinc cell development program initiated at MDC and continued at SRI, was to demonstrate that the use of separators of largely inorganic constitution, would bring longer stand and cycle life to silver-zinc cells. A derived objective was to improve these separators by modifying its composition to further extend the cell performance. Both objectives were realized. We believe that other modifications can enhance cell performance still further.

A full discussion on the finding of this study and their significance with respect to the cells fabricated by MDC and tested both at MDC and SRI (Contract NAS 3-15686) and continued in testing on the present contract are found in Reference 7. Most, if not all of the observations and comments cited in that reference apply to the cells continued in testing on the present program. An additional finding, however, relates to the zinc mush found external to the bags and filling the void areas at the bag edges (commonly in the bottom of the cell): When the seam splits occurred in both the Ag and Zn bags, and the split areas were choked with metallic zinc mush, it appears that a number of cells failed by shorting through this metallic path.

A brief summary of the discussion in Reference 7 follows. Elevated stand temperatures were detrimental to good cell performance. The attack on the organic binder of the separator coating and on the cement

bond at the separator bag edges is enhanced by elevated temperatures, tending to promote earlier failure. Conversely, as expected, lower temperatures favor extension of cell life. Cells on charged or float-charged stand likewise had shorter lives than cells on discharged stand. Moreover, cells cycled immediately after activation (VK-2 regime) displayed long cycle and wet life (Table 13). Also, cells on charged or float-charged stand (as is true for the 100% DOD cells with a 1-month charged stand between cycles) had as a significant failure mode, shorting by zinc nodules, sometimes quite early in the cycling portion of cell testing.

Bag splits (at the cemented seams) almost always were choked with active negative plate matter, and most bag splits were located in the Zn bags. In the few instances of Ag bag splits, the open areas were also choked with Zn and ZnO. On a charge portion of a cycle, it would be easy to conceive of an electronic bridge between Zn and Ag electrodes. Whether the splits originated in a delamination of the glue line, or in tears adjacent to the glue line by the invading zinc mass could not be determined. In any case, a weakness appears in this area of the separator, quite likely aided by gradual degradation by silver oxide.

Contract NAS 3-15686 had, as one of its major goals, the screening and identification of a few optimum inorganic materials to use in the separators of silver-zinc cells. The selection of materials B, JC, and S´ required the building and testing (the first series) of two-plate cells with material Q (3420-25) as a control, since the latter was used in building all the cells fabricated by MDC and tested on earlier programs as well as this program. Actual cell testing permitted the selection of the best separator composition, which proved to be the S´ material. Cells containing S´ material in the first series did not decline to or

below 50% capacity by Cycle 130, although the others had declined earlier.

The second series of tests disclosed that excessive doping was not favorable to maintaining high capacity, although it improved the suppression characteristics of zinc dendrite growths, both on the working faces and on the back faces of the separator bags. This suppression characteristic suggests that cells containing the SS separator might cycle for a long time, but at depressed capacities.

Of the materials tested on this program, S´ material proved the best, verifying the findings of the screening tests program of the preceeding contract (NAS 3-15686).

CONCLUSIONS

Original MDC Cells

The results of this testing program, continued from Contract NAS 3-10928, and NAS 3-15686, showed that MDC heat-sterilized silver-zinc cells containing proprietary semiflexible separators were able to survive at least four years (some cells on wet stand for about one-half that time before cycling) and to deliver more than 1000 cycles. Four batteries delivered more than 2000 shallow charge-discharge cycles. Thus, one of the major objectives of the silver-zinc development program was accomplished.

If cells are required to undergo an activated stand period, the discharged stand favors longer cycle and wet life over either charged stand or float-charged stand. Furthermore, continuous shallow DOD cycling immediately following activation also seems to favor long life, compared to achievable life under conditions of charged stand or float-charged stand followed by shallow cycling. Storing cells at low temperatures (for example 283°K) appears to favor higher survival.

Although the limitations of small sample statistics apply to most of the results relating to the secondary testing objectives, the following conclusions appear reasonably well established.

(1) Additional layers of separators between bags increase cell cycle life for shallow and deep cycles.

(2) Plate-locking electrodes in cells with epoxy cement reduces cell wet and cycle life. This effect is reduced as the epoxy cement is more thoroughly cured. Environmental testing does not seem to affect cycle and wet life of plate-locked cells.

(3) Operating cells as groups in "batteries" has reduced cell wet and cycle life, presumably because individual cells can experience overcharges as cell imbalances develop with age.

Cell failure analysis shows shorting by zinc nodules to be a significant cause for cell failures. However, these failures were observed only in cells that had been charged for an extended period of time and had undergone either deep discharges or significant overcharges. These failures also appeared in cells cycled immediately after activation when cycle life and wet life was high and when cells had been cycled once per month (100% DOD) with charged stand for approximately one month between cycles. Zinc nodule shorts were formed under these conditions, apparently partly because the semiflexible separators were extensively attacked by dissolved silver oxide and were unable to withstand zinc penetration.

Cell shorting by filament-type zinc dendrites appears to have caused most of the remaining cell failures, especially those that occurred after large numbers of cycles. Shorting by silver deposited in semiflexible separators was not observed in any of the cells. Although many cells developed a number of faults, such as leaks, electrode erosion, slumping and split seams, no significant correlations existed between these faults and specific failure modes, except in the case of split seams. About 20% of the 30 cells analyzed failed by shorting through the external zinc mass when both Zn bags and Ag bags in the same cell were split. Only cells of one subgroup showed a modest degree of zinc electrode slumping. This low incidence of zinc electrode slumping points to the advantage of using inorganic electrode separators to acheive extended cycle life in both shallow and deep cycling of alkaline cells with zinc negatives.

Two Plate Cells

The results of the cell testing of separator materials selected on the basis of screening tests showed that the best separator material was doped calcium zirconate (Material S′). This separator material performed best in both series of two plate cell tests, when compared to a synthetic olivine (material B), a commercial magnesium titanate (material JC), and a reference material used to build the separators of MDC cells (material Q). Material S′ was also superior to a more heavily doped calcium zirconate (material SS), and was better than commercial calcium zirconate (material P).

In the first series of tests, only cells containing separators of material S′ had more than 50% of the original capacities at Cycle 130 (100% DOD).

In the second series of tests, cells containing S′ separators had the highest average percentage of the original capacity when the tests were terminated at Cycle 120.

The following brief conclusions may be cited:

(1) The S′ separators had only minor slumping, no plate erosion and separator erosion, and few Zn nodules or Zn dendrites in or on the working faces of the separator bags. These separators maintained more of the original capacity than any of the other separators.

(2) Q separators had the most slumping, plate erosion, and zinc dendrites (and nailhead nodules) both on back faces and working faces. The capacity maintenance was second to the S′ separators in the first series of tests.

(3) SS separators showed no external Zn deposits, separator erosion, plate erosion, or slumping. The capacity maintenance was second to the S′ separators in the second test series.

(4) Including lead in the Zn electrode did not add any unique benefits to P separator performance above those benefits of normal Zn electrodes.

(5) Based on the individual studies of the pilot cell in the second series and the charge currents used, the upper charge voltage limit could be set to 2.100V without danger of excessive gassing. (Maximum pressure rise at end of charge was one to two psi (0.7 to 1.4 N/cm^2.) Increasing the upper charge voltage limit would provide a formation charge capacity approximately 50% higher than the second series average.

RECOMMENDATIONS

The results and conclusions of the cell testing programs lead to the following recommendations.

(1) If MDC-type silver-zinc cells using the present designs and semiflexible separators are to be standing for extended periods, discharged stand should be used. If charged stand is an operational requirement, the standing temperature should be 283°CK (10°C) or lower.

(2) Deep cycling (such as applied in reconditioning or in 100% DOD regimes) should be avoided for cells that have experienced extended periods on charged stand.

(3) The major cause(s) of cell capacity loss in standing and cycling should be investigated. As part of this effort (or for its own merit) the possibility of developing a "nondestructive" silver electrode capacity test based on the rate of voltage rise should be explored.

(4) Operation of cells in batteries is to be avoided unless circuitry is provided that allows cells to be removed individually from charge and discharge.

(5) The upper voltage limit for cell charging should be reliably controlled. Charging circuitry should be used that "recognizes" the voltage spike associated with the phase transition of silver (I) oxide-silver (II) oxide.

(6) The separator constituent mainly responsible for forming silver deposits should be identified, and the effect of its elimination on cell behavior and life should be investigated.

(7) Improved techniques (and their automation) for enclosing electrodes in bags should be devised. This effort should include developing better bag seals and investigating

electrodes with rounded edges that would improve current distribution and permit improved conformity of bags, thus eliminating void spaces within bags.

(8) Improved seals for terminal posts should be designed.

(9) Unless needed for specific applications, plate locks should not be used. If needed, plate locks should be made from fully cured epoxy cements or from chemically neutral, powdered resins, fusible at temperatures compatible with cell structure, thereby acting as immobilizing cements.

(10) Eliminate void spaces between the separator bags and between the cell case.

(11) The origin of polarizations, which seem to affect cell performance, and the C/2 discharge rate should be investigated so that cell performance at discharge rates higher than C/2 could be improved.

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